

SO_x RECLAIM STUDY

FINAL REPORT

MODULE 2: REFINERY FUEL GAS TREATMENT AND SULFUR RECOVERY/TAIL GAS UNITS

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I. EXECUTIVE SUMMARY

ETS/AEC were commissioned to conduct an engineering evaluation and cost analysis assessment for technologies to control SO_x emissions from refineries in the South Coast Air Quality Management District (SCAQMD). The physical scope of this study encompassed six petroleum refining companies in the South Coast area (listed alphabetically):

- BP (Carson)
- Chevron (El Segundo)
- ConocoPhillips (dual locations in Carson and Wilmington)
- ExxonMobil (Torrance)
- Tesoro (Wilmington)
- Valero (Wilmington)

The goal of the overall project was to conduct an evaluation of emission control technologies for further reducing SO_x emissions (at the major sources) from refinery fuel gas treatment and sulfur recovery/tail gas treatment units.

Outputs of the program include an evaluation of existing commercially available control technologies, starting with the most effective control technology, recommendations to SCAQMD on various technologies that could potentially be used to achieve additional emission reductions, various concentration targets that could be achieved with each technology, the estimated emission reductions, the multimedia impacts, energy impacts of the technologies, and the cost effectiveness associated with the control technology.

As a part of this project, in the three-week period beginning on the 22nd of September 2008, AEC engineers visited the six above-mentioned refineries, seeing two of them per week. The purpose of the visits was to assess the performance of the facilities' existing SO_x emission control equipment and the available space to install supplemental treatment equipment. An additional objective of the visits was to obtain emission and operational information pertinent to the successful fulfillment of the overall program objectives. A crucial part of the study has been the determination of necessary infrastructure/utility improvements triggered by SO_x reduction measures; this involved both scope and cost assessments. Similarly, it was necessary to obtain the clearest possible understanding of the often complex nature of retrofitting existing equipment.

As follow-up for the purpose of resolving any outstanding issues, a second visit was made to all but one of the refineries during the week of February 16, 2009. The following refiners were re-visited; BP (2/17), Tesoro and Valero (2/18), Chevron and

ConocoPhillips-Wilmington (2/19). These visits were conducted by Robert Kunz (ETS) and Tav Heistand (AEC), with Minh Pham and Joe Cassmassi (2/17 and 2/19) of SCAQMD in attendance.

In the final project tally, more than 150 individual measures were evaluated for cost and effectiveness. Of that total, about 30 were included in this Module 2 study.

An overview summary of the project findings for fuel gas treatment is provided below:

1. The predominant method for fuel gas treatment to remove sulfur-bearing compounds is by contact with liquid-phase solvents. This technology is currently used in every one of the refineries in the South Coast Area, and, in fact, in most of the petroleum refineries worldwide. However, the solvents employed span wide ranges of chemistry and solution strength. This study focused only on those fluids in most common use, the amine and caustic families, which have been amply demonstrated as applicable and effective over several decades. (See the general references appendix to this report for selected information about the wide range of solvent candidates.)
2. The options studied took into account the pertinent aspects of each refinery: total flow; gas composition; stream pressure and temperature; existing treatment; sulfur contents and speciation; equipment and piping configurations; etc. Those individual factors were so important, as it turned out, that the best measures were specific to the facility. It was not possible to make any universal choices. As it turned out, though, the options with the largest predicted SO_x reductions are Sulfinol (a proprietary formulation by Shell) and Merox (a customized caustic absorber system). In general terms, it can be said that the most commercially available and cost effective technologies were those that best supplemented the existing treatment methods by, for example, targeting streams with higher mercaptan concentrations via contacting with a solvent having good affinity for such molecules.
3. The net removal efficiencies for the various solvents studied are not absolute numbers, but instead depend on stream characteristics such as those mentioned above. For the purposes of quantitative comparison and estimating emission reductions, the removal efficiencies stated in the following table were used in this study:

<u>Solvent Name or Type</u>	<u>Approx. Optimum Removal Percentage</u>			
	<u>H₂S</u>	<u>Mercaptans</u>	<u>COS</u>	<u>CS₂</u>
MEA (monoethanolamine)	99.9%	20-50%	>70%	>70%
DEA (diethanolamine)	99.9%	20-50%	70-80%	70-80%
MDEA (methyl diethanolamine)	99.9%	<20-50%	10-33%	<70-80%
Caustic solution (NaOH) - Merox	90%	80-90%	10-15%	*
Sulfinol	99.95%	97%	38%	*
TG-10 (amine additive)	99.99%	<20-50%	<10-33%	<70-80%
(* Information not available.)				

The 2005 baseline concentrations of total sulfur in refinery fuel gas for the Los Angeles area refineries range from 40 to 200 ppmv. As a result of this study, AEC has determined the cost effective reductions for individual refineries' fuel gas treatment systems to be within the range of 11-102 ppmv total sulfur, dependent on the location. For all the South Coast refineries, the maximum of 40 ppmv total sulfur in fuel gas is an SCAQMD established upper limit. A 40 ppmv sulfur concentration in refinery fuel gas has already been justified as technologically and economically feasible in conjunction with Rule 431.1.¹ Although Rule 431.1 itself has been subsumed by RECLAIM for the Los Angeles area refineries, that justification is still valid, and it is the recommendation of ETS that the present value of 40 ppmv total sulfur in refinery fuel gas be retained as the Best Available Retrofit Control Technology (BARCT) level. Please see Section III. D. 2 for a more detailed discussion.

4. The measures recommended by AEC are the measures that gave the *largest expected SOx reduction potential* while also featuring the most *reasonable cost effectiveness*. **The total overall emissions reduction is approximately 0.89 tons per day SOx.**
5. **The overall cost effectiveness for refinery fuel gas, averaged over the commercially available measures that AEC recommended for the refineries in this study, is estimated to be \$16,823 per ton SOx reduced.** The study team estimates that any given cost effectiveness number has an *expected range* someplace within the band of -10% to +50%.
6. The anticipated utility and energy impacts on the refineries are widely different from one another. This topic is addressed in the facility confidential reports.

¹ South Coast Air Quality Management District, Rule 431.1, Staff Report to Amend Rule 431.1, Sulfur Content of Gaseous Fuels, April 5, 1990 ("Rule 431.1 Staff Report"). Exhibit B.

7. For refineries requiring the installation of new fuel gas treatment equipment, the space for the new installation has been addressed in the individual facility confidential reports.

An overview summary of the project findings for the SRU/TGTU systems is provided below:

1. The pre-discharge treatment of sulfur-bearing gases and vapors leaving a typical SRU/TGTU plant customarily is provided via a SCOT, Wellman Lord, or Stretford unit. That tail gas unit, coupled to the back end of an SRU Claus train, gives very good sulfur removal, and has been doing so in a variety of plants for decades. Nowadays, however, several processes have been proven to achieve even more efficient sulfur capture. They include, among others: the addition of extra Claus reactors; sub-dew-point Claus converters; proprietary catalytic gas treaters (like EmeraChem's ESx process); and alternative solvents (e.g., specialized additive TG-10) for absorbing sulfur out of the tail gas.
2. The options studied took into account the pertinent aspects of each refinery's sulfur plant(s), especially including the existing overall sulfur removal efficiency and the specific process configurations. Generally, though, the measures with the largest potential SOx reduction amounts fell into one of two categories: utilization of sub-dew-point sulfur production or the treatment of tail gas in a special contactor application.
3. One way in which to compare SRU/TGTU treatment systems is not in terms of outlet SOx concentration, but rather as net removal efficiencies based on the total sulfur feed into the SRU and the sulfur remaining in the tail gas stream after passage through the SRU. The following removal efficiencies tabulated in the table below were used to determine emission reductions in this study:

<u>Technology or Measure</u>	<u>Approx. Optimum Removal</u>	
	<u>Percentage</u>	<u>Based On</u>
Add 3 rd Claus reactor to train with only two reactors	98%	SRU sulfur
HydroSulfreen process	99%	SRU sulfur
EmeraChem ESx	99.5%	tail gas sulfur
TG-10 amine special additive	99.99%	tail gas sulfur

Notwithstanding the above considerations of sulfur removal efficiency, ETS is able to generalize the results of this study in terms of ppmv SOx or reduced sulfur species remaining in the sulfur plant tail gas.

Except for one refinery, whose SRU tail gas is regularly vented, and another refinery whose combustion device is considered by the refinery not to be a treatment / control device of the tail gas unit, the 2005-baseline SO_x in the SRU is about 100 ppmv (@ 0% O₂) or less. These figures are well below the 40 CFR 60 Subpart J (or Ja) standard of 250 ppmv SO_x (@ 0% O₂).

Guaranteed outlet SO_x concentrations of 5 ppmv after scrubbing can be achieved, in the worst case at 95% SO_x removal efficiency; in most cases, the required scrubbing efficiency for a 5-ppmv SO_x outlet is considerably less.

Except for the two aforementioned refineries, it has been found possible in this study also to reduce SRU ppm SO_x to the atmosphere by the gas treating techniques investigated. Those results are all below 10 ppmv, and in many cases below 5 ppmv.

The ETS recommendation for SRU/TGTU emissions is therefore as follows:

- For uncombusted tail gas, the limits of Subpart J (Ja), namely 10 ppm H₂S and 300 ppm reduced sulfur species (total of H₂S, COS, and CS₂), should continue to apply. Refineries should be encouraged to reduce emissions so as to be able to vent rather than having to combust SRU / TGTU tail gas.
 - For combusted / incinerated tail gas, 5 ppmv SO_x @ 0% O₂ should be defined as the overall BARCT level for all refineries, based on scrubbed flue gas, but permissible to achieve by whatever means possible. A level of 10 ppmv would allow a greater number of refineries to meet the overall BARCT level by the gas treatment methods of Module 2 without having to install a wet gas scrubber (Module 3A). See Section III. D. 4 for a more detailed discussion.
4. As a result of the effectiveness of some TGTU scrubbing applications studied in module 3A, only a portion of the recommended treatment measures for SRU/TGTU are module 2 measures. The study recommendations can be found in the individual (confidential) refinery reports. A significant amount of SO_x (ranging between about 75 and 290 pounds/day) can be captured by the implementation of the commercially available and most cost effective module 2 treatments in the respective SRU/TGTU plant(s). **The total estimated SO_x reduction resulting from the Module 2 recommended measures from the refineries is approximately 0.31 tons per day.**
 5. The cost effectiveness metrics for the recommended module 2 treatment measures at the corresponding refineries have a very wide range: from as little as \$13k up to over \$54K per ton of SO_x. The actual spectrum of realized values, though, will probably be much broader. Therefore, the study team estimates that any given cost effectiveness number has an *expected range* someplace within the band of -10% to +50%. **The overall cost effectiveness, averaged over the commercially available**

module 2 measures that AEC recommended for the refineries in this study, is estimated to be \$21,853 per ton SOx reduced. The measures recommended by ETS/AEC are the measures that gave the *largest expected SOx reduction potential* while also featuring the most *reasonable cost effectiveness*.

6. The anticipated utility and energy impacts on the refineries following implementation of the recommended treatment measures are widely different from one another. See the facility (confidential) reports for details.
7. For the refineries requiring the installation of new SRU/TGTU equipment, the space for the new installation has been addressed in the individual facility confidential reports. For the remaining refineries where the recommended measure is merely the replacement of the existing solvent with a new one, or the addition of a special additive to the system, plant space will probably not be a factor.

FINAL RECOMMENDATION BY ETS FOR BOTH MODULE 2 & MODULE 3A

Table EX-1 and EX-2 give a final recommendation of the total SOx emission reductions and average cost effectiveness ratios by refinery following implementation of the respective measures selected by ETS/AEC in both Modules 2 and 3A.

Table EX-1

Forecasted SOx Reductions (tons/day) by Refinery

<u>Refinery:</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>Total</u>
<u>Equipment Type</u>							
FCCU	0.58	0.19	0.28	0.20	0.87	0.94	3.07
SRU/TGTU	0.13	0.17	0.15	0.04	0.06	0.29	0.83
Fuel Gas	0.06	0.07	0.04	0.35	0.33	0.04	0.89
<u>Htrs/Blrs/etc.</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>0.00</u>
All Above Types:	0.77	0.43	0.47	0.59	1.26	1.27	4.78

Table EX-2

Cost Effectiveness (\$/ton of SOx) by Refinery

<u>Refinery:</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>Avg. for All</u>
<u>Equipment Type</u>							
FCCU	\$14,437	\$76,211	\$36,636	\$42,103	\$11,600	\$12,849	\$24,572
SRU/TGTU	\$22,410	\$39,000	\$12,881	\$54,686	\$123,186	\$36,359	\$37,412
Fuel Gas	\$2,395	\$30,948	\$46,905	\$4,903	\$21,071	\$57,428	\$16,824
<u>Htrs/Blrs/etc.</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>
All Above Types:	\$14,770	\$54,303	\$29,982	\$20,975	\$36,025	\$19,643	\$25,533

Appendix A, Table A-1 has a summary of 2005 baseline emissions, estimated emission reductions, and theoretical remaining emissions for each refinery. Appendix A, Table A-2, has a summary of the measures in Module 2 and Module 3A selected by ETS/AEC for this project applicable for each refinery, and the estimated cost effectiveness ratios for each refinery.

ETS believes that it is conceivable that an emission reduction of 4.78 tons per day can be achieved from the refineries implementing the commercially available measures described in this project within a construction time frame of approximately 3 calendar years or less following the completion of study designs and engineering.

One refinery has already installed a wet gas scrubber on its FCCU regenerator. As such, the opportunities to reduce SO_x emissions at its FCCU are virtually nil for this refiner. However, the estimated SO_x reductions (derived from the 2005 baseline number and an outlet concentration of 5 ppmv) and cost effectiveness ratio (estimated from refinery and overall study data) were included for comparison. It should be noted that the cost effectiveness ratio for this refinery was not included in any of the average cost effectiveness calculations.

II. FACILITY & EMISSIONS PROFILES

A. GENERAL FACILITY & EQUIPMENT DESCRIPTIONS

Each of the South Coast refineries processes a variety of feedstocks—typically crude oils—into several hydrocarbon products. The most common of the latter are automotive (gasoline and diesel) and aviation (e.g., jet) fuels, all of which have tight upper limits on the allowable sulfur contents. (A broad spectrum of other products and by-products is also produced, but they are of lesser volume and/or importance than the preceding transportation fuels.) However, the refinery feeds—with quantities in the many thousands of barrels per day—often contain significant percentages of sulfur. The average weight content of sulfur in common domestic and Western Hemisphere crude oils commonly exceeds 1%, and can occasionally be above 3%. That represents a large daily quantity of elemental sulfur. In fact, the average production of sulfur from the refineries is greater than 200 long tons per day per refinery.²

² This number was provided to AEC directly by the refineries during the site visits in September-October 2008.

Given that the maximum permissible sulfur levels in the above-mentioned transportation fuels are measured in at most the 10's of parts per *million*, it's clear that sulfur removal from the crude oil (and other) refinery feeds must be extremely thorough. The primary method for achieving that feed desulfurization is by hydrogenating (more often referred to as "hydrotreating") the sulfur in the process stream; in other words, elemental hydrogen is encouraged to bond with the sulfur atoms in a 2:1 ratio, creating hydrogen sulfide (H_2S). (Optimizing that process ordinarily requires high pressures and temperatures, plus the presence of a suitable catalyst, as well as an abundance of hydrogen.) Subsequently, the gaseous H_2S (along with a host of other low molecular weight and volatile substances) is separated from the main hydrocarbon stream, leaving it with a much lower sulfur content than was in the feed.

The mixed-species gas stream mentioned above, containing the H_2S , is most often sent to an absorber (or contactor) vessel, where it is exposed to a liquid (such as an amine/water mixture) which is chosen for its tendency to absorb H_2S , and sometimes other sulfur species. The absorption of the gases transforms the "lean" solvent to a "rich" one. Next, the latter liquid is regenerated (i.e., processed so that it relinquishes the H_2S which was absorbed from the incoming gas stream) in a separate vessel with heat, making it back into lean solvent, suitable for recycling to the absorber/contacter. Meanwhile, the rejected gas, expected to be high in H_2S , is exported to a separate unit—the Sulfur Plant/Sulfur Recovery Unit (SRU). In that unit H_2S is reduced to elemental (molten) sulfur in a well-known series of chemical reactions using air and/or pure oxygen and facilitated by one or more special catalysts. The SRU consists of a Claus Plant in which 90-96% of the sulfur is removed at a "back end section" known as the Tail Gas Treating Unit (TGTU) which addresses the residual sulfur compounds not removed in the Claus Plant.

The TGTU takes the residual vapors from the SRU, still containing sulfur-bearing compounds, and attempts to extract more of the sulfur—usually as H_2S —for recycling back to the front of the SRU (some TGTU processes utilize a direct oxidation or reduction step via a specialty catalyst and convert the H_2S directly to sulfur). But at the very end of most TGTU processes, the effluent (non-recoverable and non-recyclable) gas stream is disposed of to the atmosphere by either free venting or by combustion in a thermal oxidizer or incinerator. If combusted the sulfur in that effluent gas is oxidized to SO_x —that is, mostly SO_2 . When designed and operated well, the overall conversion efficiency of sulfur in the SRU/TGTU feed to the captured sulfur within it is substantially better than 99.8%.

Overall, every one of the refineries is already achieving very high efficiencies—in terms of general industry benchmarks—for the removal of sulfur from feedstocks and, more

importantly for this study, for the conversion of vapor-phase sulfur compounds into by-product molten sulfur. Therefore, the percentage of feed sulfur that is ultimately released to the atmosphere as SO_x is quite low: typically in the neighborhood of 0.2% or less. But when the net inflow of elemental sulfur is greater than 400K pounds per day, an approximate SO_x emissions rate of more than 1600 pounds per day, or 0.8 tons per day (assuming 99.8% net removal, a molecular weight of 32 for elemental sulfur and 64 for SO_x, respectively), would result. That is clearly a substantial contribution to the South Coast stationary-source atmospheric SO_x burden. In fact, as shown in the SCAQMD Preliminary Draft Staff Report, Table 5-2, the SO_x emissions from the SRUs/tail gas systems were even larger than 0.8 tons per day; that table indicates approximately 0.96 tons per day in 2005, 1.02 tons per day in 2006, and 0.96 tons per day in 2007. While the area refineries may be performing better than most worldwide refineries insofar as the release of SO_x is concerned, the technologies employed are not, in all cases, fully optimized. And that means, in essence, that the application of certain technological improvements may noticeably reduce the overall SO_x emissions from the six operating companies being investigated in this project.

Today, each refinery in the South Coast area employs multiple amine absorber vessels in which various refinery gas streams are contacted for sulfur removal; the primary target sulfur species, and the one most effectively removed, is H₂S. In a few cases, treatment with a Merox (i.e., caustic solution typically preceded and/or followed by suitable sponge oil absorption) unit is provided for a portion of the fuel gas network. That Merox system is somewhat more effective than the traditional MEA and DEA solvents for capturing sulfur in the form of mercaptans and other non-H₂S species.

Generally speaking, once the multiple refinery gas feeds are passed through the site's relevant absorbers, the individually treated streams are combined into the common "refinery fuel gas" system, for distribution by a branching piping network to the many refinery users. As a general—but not universal—rule, the refinery fuel gas system is also equipped with one or more points for inflow of natural gas, typically on a pressure-controlled basis. Also common are special users (e.g., those requiring lower sulfur fuel) that receive dedicated fuel gas supplies composed of higher proportions of natural gas and/or segregated streams of process-derived fuel gas.

B. EMISSION PROFILES IN 2005 & 2008

The total reported SO_x emissions from the subject refineries since 2004, and up to the present, spans a range from about 0.8 to nearly 2 tons/day per refinery. There is a decline in emissions from 2005 to 2008 (based on partial year-to-date totals made available to the

study team), at least with respect to some of the refineries. This is definitely encouraging, and probably the direct result of multiple efforts being made to achieve better environmental controls. For example, one of the refineries recently installed and commissioned a wet gas scrubber for its FCC regenerator exhaust; this investment has already had measurable—even dramatic—impacts in cutting total SO_x emissions. Likewise, the increased application of SO_x-reducing catalyst additives to the FCC units in other refineries has had beneficial impacts on the SO_x totals.

When it comes to the question of how individual system or point sources of SO_x contribute to the totals, the picture is a little different for each refinery. In almost all cases the FCC is the biggest single emitter. Typically, after that, the categories of (a) fired equipment (i.e., heaters, furnaces, boilers, and cogeneration units) and (b) sulfur recovery units (SRUs, including TGTUs) are the next most significant emission categories. As mentioned above, the cumulative SO_x emissions from the SRU/tail gas systems were about 1 ton per day from 2005 through 2007. And, as shown in the SCAQMD Preliminary Draft Staff Report, Table 4-2, the SO_x emissions from the top emitting boiler/heaters were approximately 0.91 tons per day in 2005, 0.98 tons per day in 2006, and 1.11 tons per day in 2007.

III. CONTROL TECHNOLOGIES—FEASIBILITY ANALYSIS

A. CRITIQUE ON SCAQMD PRELIMINARY DRAFT STAFF REPORT

The “Preliminary Draft Staff Report for SO_x RECLAIM (Part 1)”, dated 3 April 2008, was an immensely informative document. Clearly described therein were probably the most obvious—if not also some of the most important—candidate technologies for SO_x reduction in each one of the systems being investigated by AEC. Moreover, the report was exceedingly helpful in its identification of certain manufacturers and their respective packages for the referenced technologies. Yet other valuable inclusions were the comparisons of efficiency ranges for treatment types.

While the April report was an excellent starting point for the evaluations, it was neither intended to be, nor was it used as, a completely prescriptive guideline for the work. The basic technologies enumerated in that document were fully explored, but the engineering efforts didn’t stop there. The general principle for this study is simply stated as follows: The goal was to identify and quantify (in terms of cost and benefits) the best technologies for SO_x reduction in the refineries, provided they were practical and proven. In doing so, certain named approaches were considered. However, beyond that, AEC inferred from

the materials obtained from the SCAQMD that the investigation should explore other viable methods, as long as they passed the general tests of being technically practical; effective; reliable; and verifiably able to meet their performance requirements. In that vein, the AEC team members conducted very broad-based research and brainstorming to come up with the best opportunities.

B. LITERATURE RESEARCH ON CONTROL TECHNOLOGIES

The extent of the team's general research was initially limited to the acquisition of basic data on the primary SO_x reduction technologies. That data was used to generate "briefing sheets" and field checklists taken to the refineries for the initial visits. The AEC engineers were, therefore, able to maximize the effectiveness of their short times in the refineries. That research, fortunately, largely constituted updating of information and contacts which had already been accumulated by AEC and its parent company, IDOM, over the past few decades of work in refineries and power plants. Through those previous projects by AEC and IDOM—and others which were contemporary, for a variety of worldwide clients—we had access to reliable and recent applications of proven technologies for the reduction of SO_x emissions. Particular examples of those technologies were both wet and dry scrubbing, as well as the latest generations of gas treating methods and the variants to the traditional Claus/SCOT sulfur plants. Nevertheless, in spite of this extensive resource base, the team validated all the pertinent details and, of course, updated them to the relevant design parameters under which the South Coast refineries' units were functioning at that time.

Once the trips were completed, AEC screened and prioritized all of the SO_x reducing technologies for particular systems and equipment items. This was a very extensive task, requiring a huge amount of particular data for the candidate packages. The veins of AEC's research included media such as: periodicals; textbooks; the Internet; internal corporate files; telephone calls; and manufacturers' literature.

Assimilating all the technology-related information helped the evaluators compile all the relevant features and impacts of each candidate technology, relative to its intended installation point. And, as a consequence, AEC is able to present an assessment, following the methodology prescribed by the AQMD, of both (a) the costs of installation and operation, and (b) the net operations impacts (including, most importantly, the expected SO_x reductions for the stipulated levels of controls, along with any changes to other pollutant emissions) for the technologies under consideration. With that information available, all the stakeholders are better positioned to make the important decisions about what technology retrofits and additions are the most reliable, effective, and affordable.

Opportunities that were evaluated, along with the primary reasons for them being considered, are provided below:

- Modified routing of sulfur-bearing vapors to ensure either different or simply more effective treatment to remove the relevant sulfur species. Likewise, this measure did find direct application in a few locations, and was included in the respective refinery confidential reports.
- Additional new stage/unit in the SRU/TGTU for improved sulfur recovery. This measure yielded significant sulfur recovery potential; however, the costs associated with it were very large. This measure is also included in the respective workbooks.
- Stack treatment of TGTU tail gas to capture H₂S and SO_x. This measure proved very effective with respect to cost and sulfur removal for some refineries and is worthy of further evaluation.
- Solvent swap/addition to improve sulfur recovery in amine absorbers. This measure proved very effective with respect to cost and sulfur removal for some refineries and is worthy of further evaluation.
- Additional new gas-phase Merox unit to treat some, or all, of the refinery fuel/off gas. This measure yielded significant recovery and cost effectiveness in some cases (essentially refineries with streams containing large mercaptan concentrations). It is worthy of further evaluation for some of the refineries.

C. IDENTIFICATION OF RELEVANT VENDORS AND CONTACT STATUS

Efforts to capture all the potential vendors and licensors of applicable treatment systems constituted a large portion of the total work scope. Hundreds of man-hours were expended to capture information about the best prospective manufacturers and how their systems could contribute to SO_x reductions. All that knowledge was used to create the reports' detailed matrices and summaries.

D. DISCUSSION ON CONTROL TECHNOLOGIES & POTENTIAL EMISSIONS REDUCTIONS

1. FUEL DESULFURIZATION

The six refinery fuel gas systems run the gamut when it comes to sulfur content: from just over 40 ppm in 2005 to in excess of over 200 ppm. It is readily apparent that those facilities with the higher concentrations of sulfur in their refinery fuel gas systems are going to emit relatively more SO_x, all else being equal. And the absolute amount of emissions is proportional to both the concentration and the total amount of gas burned in refinery equipment. Since none of the facilities are allowed to regularly flare excess fuel gas, essentially all of the fuel gas that's produced is ultimately burned, converting each mole of sulfur into a mole of SO_x. Therefore, the bottom line is that SO_x emissions from equipment burning refinery fuel gas will drop in the same ratio as the total sulfur content in that fuel stream is reduced. A properly implemented treatment scheme will enable some refineries to obtain sizeable net SO_x reductions. This is especially true if they experience relatively high sulfur contents now, coupled with large volumes of produced refinery gas.

Certainly for all of the combustion equipment encountered in a refinery, an *effective* one-to-one savings in SO_x emissions will result for every reduction in sulfur content in the fuel stream. (To be precise, for every *mole* of sulfur (S) removed from the fuel supply, a *mole* of SO_x will be absent from the exhaust gas, assuming, of course, that there is ample oxygen for full combustion and that no post-combustion SO_x reduction technology will be installed. And since SO_x is predominantly SO₂, the extraction of a pound of atomic sulfur from the fuel will drop the SO_x inventory in the exhaust gas by approximately 2 pounds.) Thus, there is a strong incentive to minimize the sulfur concentration in any fuel sent to a burner assembly.

The refineries already treat nearly all of the gas feeds (except for natural gas) into the refinery fuel gas networks. Since that treatment customarily takes place in an amine absorber (or in equipment of at least comparable effectiveness), which has good selectivity for hydrogen sulfide (H₂S), the outlet gas usually has a relatively low H₂S concentration. But other sulfur compounds—like carbonyl sulfide (COS), carbon disulfide (CS₂), and mercaptans—are not equally absorbed out of the gas stream. Caustic scrubbing is the typical treatment method for removing the non-H₂S sulfur compounds among the refineries.

Of course there are many subcategories to the sulfur recovery measures listed above. For example, there are several types of amines, each with its own characteristic sulfur removal efficiency. One of the objectives of this study was to identify the most efficient method for absorption of the aforementioned non-H₂S species and to increase, where possible, and otherwise maintain the already efficient H₂S capture. The possible methods, with respect to amine treatment, included replacing the current amine with a new high-efficiency amine, adding one or more amine absorbers/regenerators, and including an additive in an already functioning amine system to increase efficiency. Treatment of the entire fuel gas system and localized treatment, targeted to streams containing relatively high levels of sulfur, were both considered. Amine treatment will be discussed in greater detail below.

For each potential measure, only proven refinery technologies were considered. Information for each technology was gathered via internet research, communication with manufacturers, licensors, and vendors, and consultation with industry experts (through the six respective refineries and among ETS/AEC/IDOM). The information that was gathered was used to evaluate the potential SO_x reductions and cost impacts. Site-specific and qualitative information was collected to initially determine which measures were feasible for each refinery. Each of the feasible measures was then evaluated using vendor/manufacturer/licensor supplied data and/or published removal efficiencies and performance data. This dictated the development of each cost estimate and effectiveness ratio. Detailed summaries for each refinery fuel gas desulfurization technology category are provided below.

AMINE TREATMENT

Considerable research was done to evaluate the best possible treatment for H₂S removal. It is common knowledge that amine scrubbing is the most effective method for H₂S removal from fuel gas, but there are many types of amines. Primary, secondary, and tertiary amines are the three main categories. The descriptor refers to the number of branch functional groups that lend steric hindrance to the amine receptor. In other words, the number of branch functional groups directly affects the reaction rate between the amine and acid gases. By adding branches and increasing steric hindrance, the relative rates of absorption of various acid gases can be optimized such that H₂S is absorbed preferentially over other acid gases, such as CO₂. Another advantage to using tertiary amines is the large solution concentration that is possible, with respect to primary and secondary amines. For example, the tertiary amine, methyldiethanolamine (MDEA), can be safely circulated as a 50 wt% solution. The larger concentration increases the H₂S removal efficiency and minimizes the required circulation volume.

In addition to pure amine systems, there are several types of commercially available amine mixtures and additives to amine systems that can be tailored to specific refining applications. Two of those are Sulfinol and TG-10. Literature values for the efficiencies of removal for H₂S using MDEA and TG-10 are 99.9% and 99.99%, respectively. TG-10 is extremely selective and removes H₂S more effectively than the pure amine, MDEA. Some amine solutions are available for purchase with TG-10 already added.

The Sulfinol process is licensed by Shell and is used extensively to treat natural gas, refinery fuel gas, coker off-gas, and synthesis gas (a mixture of CO and hydrogen). The Sulfinol process employs a mixed solvent composed of sulfolane (tetrahydrothiophene dioxide) and an alkanolamine, usually diisopropanolamine (DIPA) or MDEA in aqueous solution. Sulfolane is capable of removing carbonyl sulfide (COS), mercaptans (RSH), and alkyl sulfides in addition to the H₂S removed by a typical single amine system. Sulfinol has a removal efficiency of 99.95% for H₂S, almost as high as that of TG-10. It also has the added benefit of removing mercaptans with 97% efficiency, making it superior to other amine treatments in cases where the mercaptan content of a stream is significant.

As of 1996, Shell reports more than 180 commercial units in operation or under construction [1]. The Shell brochure, apparently published later, cites 130 U.S. units and 200 worldwide [2]. With over 200 Sulfinol units in operation, this technology is well established in the petrochemical industries. That same brochure lists 6 applications specifically mentioning refinery fuel gas in petroleum refineries.

REFERENCES

1. Kohl, A.L. and R.B. Nielsen, "Gas Purification," 5 ed., P.1225, Gulf Professional Publishing, Houston, TX (1997).
2. Shell Global Solutions (US), "The Sulfinol Process," 2-page Brochure (undated).

Because fuel gas often contains significant mercaptan concentrations, Sulfinol was considered for treatment of fuel gas systems in many cases. In other cases, where MDEA was used throughout the refinery for amine treatment, addition of TG-10 was considered as a fuel gas treatment because of projected economic efficiency. TG-10 was primarily considered as a measure for improving the sulfur recovery in the TGTUs, where virtually all of the sulfur compounds are H₂S.

In general, the overall SO_x reductions for the amine treatment measures were determined by identifying the untreated speciated sulfur content of the targeted stream using data provided by the refineries. Published and/or vendor supplied performance data for the

proposed measure was then used to determine the relative SO_x savings as compared to the corresponding refinery's current fuel gas desulfurization performance.

CAUSTIC TREATMENT

Many of the refineries treat specific mercaptan-rich streams with a caustic scrubber. UOP, a leader in the industry, licenses a caustic scrubbing technology called Merox. Merox is an acronym that stands for mercaptan oxidation. The Merox process is extremely well known in the petrochemical industries. In fact, it has become an industry standard.

One type of Merox technology, which is discussed here, is used to remove mercaptans from gaseous hydrocarbon streams. In a Merox system, NaOH extraction is used to absorb low molecular weight mercaptans and convert them to sodium mercaptides. The spent caustic is regenerated by converting the mercaptides to disulfide oil and caustic soda in the presence of air, water, and catalyst. The disulfide oil can be blended to various streams within the refinery. In many cases, it may be fed to hydrotreating for ultimate recovery in the SRU. Removal efficiencies gathered from verbal conversations with UOP representatives are approximately 90%+ for methyl mercaptans and 80% for ethyl mercaptans. To achieve those removal efficiencies, upstream amine treatment is required. The amine scrubbers remove most of the H₂S. The Merox removes most of the mercaptans and residual H₂S. This measure was either recommended for the entire fuel gas stream or for local treatment, depending on refinery-specific conditions. A detail of this measure is depicted below in figure 2.2. If a refinery had what was known or suspected to be a significant proportion of its fuel gas sulfur in the form of mercaptans, or had various sources of mercaptan streams feeding into the fuel gas mix drum, then an overall treatment was evaluated. Otherwise, AEC targeted the streams with the highest mercaptan content and evaluated Merox treatment in those particular streams. This approach was used so as to help identify the best opportunities for reducing SO_x emissions from the refineries. It also served as a means for prioritizing the finite project resources searching for the best opportunities. In some cases, detailed composition data for the fuel gas stream was not available, and estimates were used in lieu of detailed data.

Merox Process for Gas Extraction

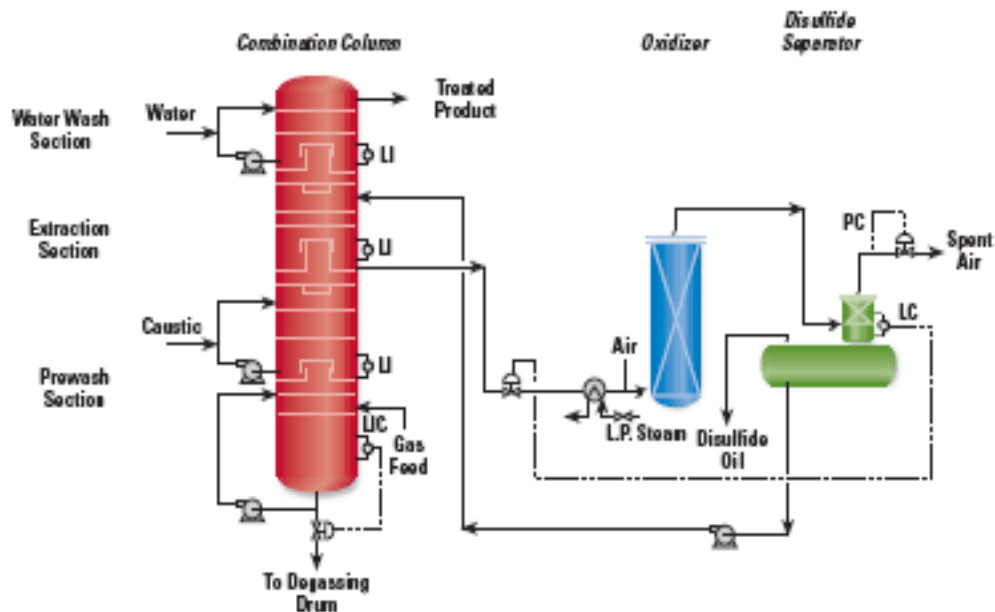


Figure 2.2: Detail of Merox process for gas extraction taken from <http://www.uop.com/objects/Merox%20Gas%20Extrac.pdf>

In general, the methods used for determining the overall SO_x savings for the caustic treatment measures were practically identical to the amine treatment measures. The slight differences were as a result of the Merox units being new stand-alone units and the variations, as compared to the amine measures, in removal efficiencies of specific sulfur compounds. Because the Merox units were all new additions, only the current speciated sulfur content of the targeted stream was needed. Published and/or vendor supplied data was then used to determine the corresponding sulfur removal efficiency and, subsequently, the overall SO_x savings. Because caustic and amine vary with respect to the capture of specific sulfur molecules, the overall SO_x reduction was highly dependent on the composition of the targeted stream.

The SO_x reduction capacities for the measures related to fuel gas treating range from under approximately 1 ton per year and up to approximately 127 tons per year. The cost effectiveness ratios also vary widely. For some installations, cost effectiveness ratios are approximately \$2400 per ton. At the upper end of the range, it can be as costly as approximately \$790K per ton to reduce SO_x emissions.

The most effective measure, with an effectiveness ratio of between \$2,000 and \$2,500 per ton, is the addition of TG-10 to existing amine treating systems. The low effectiveness

ratio (which is good) results from several factors. The required volume of TG-10 is 5 – 10% of the existing MDEA system fluid weight. Thus, a relatively small amount of capital is needed for the initial fill. It was assumed that the refineries would either be able to handle a 10% volume increase, or they would just replace the required amount of MDEA with the TG-10 additive. The disposal costs for the spent MDEA would probably be inconsequential. The only piping modifications would be the addition of an injection point, a small rotary pump with spare, and some tubing. It was assumed that the holding vessel for the TG-10 would be a tote provided by the manufacturer. Some allowances were made for civil work, but overall the cost impacts were minimal. As for the estimated SO_x reductions, the removal efficiencies were interpreted literally. Thus, an increase from 99.9% removal efficiency for MDEA to 99.99% removal efficiency for TG-10 yielded an overall capture of 90% of the remaining H₂S in the treated fuel gas. Though the opportunities to install this technology in fuel gas systems in the SCAQMD area region are limited, in some cases with the simple addition of TG-10 it may be possible to reduce SO_x emissions by over 20 tons per year.

The replacement of existing amine systems with Sulfinol is the next most effective based on the results of this study. Sulfinol is a tailored amine mixture, specific to the corresponding acid gas stream which it is intended to treat. The most attractive feature about this amine mixture is that, if desired, it is extremely efficient in removing light mercaptans, as well as H₂S. This is made possible by the addition of Sulfolane, originally developed by Shell. Based on a generic acid gas stream characterization, Shell quoted H₂S and mercaptan removal down to 5 ppmv and stipulated that Sulfinol is as good as, if not better than, MDEA at H₂S removal. As a result, the “Sulfinol swap” was considered for all types of amine treatments (i.e. MEA, DEA, MDEA, local, and global). The increase in cost with respect to the addition of TG-10 is a result of new equipment, absorber retrofit, and absorbent costs associated with the Sulfinol swap. A significant portion of the overall capital expenditure was allocated to the purchase of new amine circulation pumps because, in many cases, the overall recirculation rate may change when absorbents are swapped. New column internals were budgeted to allow for absorber retrofit (i.e. additional trays, new liquid distributors and mist eliminators, etc.). Additionally, the overall volume of the fill is much larger than that of TG-10.

The costs per ton for SO_x reduction using this technology vary widely, from approximately \$5000 to about \$790,000. The average cost per ton of SO_x reduction using Sulfinol was roughly \$20,000 per ton. While more costly on average than an addition of TG-10 to the fuel gas treaters, Sulfinol may show a greater capacity for SO_x emissions reduction in cases where substantial amounts of untreated mercaptans are present.

With both the Sulfinol replacement and the addition of TG-10 to existing fuel gas treaters, more study is necessary to completely understand the costs and benefits of these measures. Adding TG-10 to the fuel gas treating equipment, swapping existing amines for Sulfinol, or any other amine modification may require changes in circulation rates, column internals, metallurgy, heat duty, and other factors that cannot be fully determined without detailed study. These items may change the cost effectiveness and net removal rates of SO_x for measures related to amine system modifications.

Also studied was the addition of Merox treaters in the fuel gas systems. This was the most costly measure for reducing the sulfur content of the refinery fuel gas streams. The major reason for this cost differential is that the other measures have been able to rely on existing equipment in the refinery. Each Merox measure is a stand-alone unit, requiring completely new equipment. Therefore, every discipline category, with respect to the cost estimate, is increased. There will be more demolition, retrofit, and civil/structural work, but the most significant expense is the new equipment. The range of effectiveness ratios was approximately \$20K to \$165K per ton. In cases where a specific mercaptan rich stream could be targeted, a large overall sulfur removal target could be estimated with an effectiveness ratio near the low end of the range. This measure was frequently evaluated as an option along with Sulfinol. For the cases we evaluated, Sulfinol is a more cost effective way (overall) to remove mercaptans from a gas stream. However, the specific details of any particular refinery installation will determine the most aggressive and most cost effective SO_x reduction technology for those circumstances.

GENERAL DISCUSSION & CONCLUSION

Three technologies (TG10 Amine additive, Caustic Merox, and Sulfinol) have been studied in the general area of fuel gas desulfurization. They have been estimated to potentially reduce SO_x emissions from the South Coast area refineries in an approximate range of 1 to 127 tons per year per installation. The costs associated with the reductions in emissions fall in a range roughly between \$2400 per ton and up to almost \$790K per ton.

Of the technologies for fuel gas desulfurization studied, the one with the best cost effectiveness is the addition of TG-10 to existing amine systems. It is also the technology with the smallest range of potential applications. While in certain circumstances, the costs of desulfurizing fuel gas can be approximately \$2400 per ton, not all refineries can take advantage of this technology and there may be modifications to the refinery that have not been fully understood. Further study is recommended to confirm the assumptions in this study regarding requirements for new equipment to support changes

to pumping rates, equipment metallurgy, heat duties, column internals, and other potentially affected aspects of the system.

The next most economically attractive measure is the swapping of existing amines to a tailored amine mixture, Sulfinol, which is exceedingly good at removing non-H₂S sulfur compounds, particularly mercaptans and COS. This measure appears to have more applicability than the addition of TG-10, but generally comes at a higher cost. Many of the same concerns regarding confirming assumptions made in the study for the addition of TG-10 to the amine system are shared by this measure.

The most effective measures (in terms of potential for total SO_x reduction), in general, are the installation of new Merox treating and Sulfinol treatment. While Sulfinol yields the largest single SO_x reduction (approximately 127 tpy), Merox treatment consistently provides substantial overall SO_x reductions. However, Merox is also the highest cost measure, in general.

The following table summarizes the Module 2 study results, including the identification of the recommended treatment measures chosen for the refineries' fuel gas systems:

<u>Treatment Method</u>	<u>Annual SO_x Reduction (tons/year)</u>	<u>Capital Cost (\$MM)</u>	<u>Cost Effectiveness (\$/ton SO_x)</u>
Solvent additive	23.2	\$0.5	\$2,395
Added gas treater	25.2	\$15.5	\$30,948
Solvent conversion	14.5	\$22.6	\$57,428
Solvent conversion	12.8	\$11.7	\$46,905
Added gas treater	106.2	\$43.8	\$19,688
Solvent conversion	14.7	\$9.5	\$31,035
Solvent conversion	<u>126.7</u>	<u>\$12.7</u>	<u>\$4,903</u>
TOTALS:	323.4	\$116.3	\$16,823

Assuming that the refineries would implement the commercially available treatment measures, identified above, recommended by ETS/AEC for fuel gas, the overall emission reductions would be 323.4 tons per year (0.89 tons per day) at an average cost effectiveness of \$16,823 per ton SO_x reduced (within -10% +50%).

2. ETS RECOMMENDATION FOR FUEL DESULFURIZATION AND FLUE-GAS SCRUBBING

Definition of Terms

The definition of Best Available Retrofit Control Technology (BARCT) appears in the April 3, 2008 Preliminary Draft Staff Report; namely, "...best available retrofit technology means an emission limitation that is based on the maximum degree of reduction achievable, taking into account environmental, energy, and economic impacts by each class or category of source."

Refinery Fuel Gas

Refinery Fuel Gas (RFG) is a leftover stream containing gaseous-phase constituents judged not to be able to be recovered economically for sale as products. It can consist of numerous hydrocarbons, hydrogen, carbon oxides (CO and CO₂), and various sulfur species, such as hydrogen sulfide (H₂S) (primarily), carbonyl sulfide (COS), carbon disulfide (CS₂), and possible mercaptans (RSH). Thioethers (RSR') and disulfides (RSSR') may also be present. The sulfur species originate from the sulfur contained in organic compounds in the crude oil processed by the refinery.

The RFG is burned for energy in lieu of recovery as useful products. It is consumed in the refinery's boilers, furnaces, and fired heaters to make steam or raise the temperature of refinery process streams. It may be burned locally in the unit where it is generated or sent to one or more refinery fuel headers. In these days of environmental awareness, the sulfur content must be removed or reduced before combustion or scrubbed out of the resulting flue gas. Much of the RFG to be treated results from hydrodesulfurization, or hydrotreating, of refinery feed and/or product streams.

Typical treatment consists of absorption of H₂S in a continuous regenerable amine process using a reagent such as monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA), or diglycolamine (DGA). The cleaned gas goes on to become fuel. When the so-called *rich* amine solution is steam stripped in a separate regenerator vessel, the effluent gas, concentrated in H₂S, is sprung from solution, and the resulting *lean* amine solution returns to the absorber vessel for another pass.³

³ Notwithstanding the popularity of an amine process, other possibilities exist such as hot potassium carbonate, Rectisol (methanol-based), Selexol, and Sulfinol. The SCAQMD's RFP also mentions Merox. Another technology that could be used in combination with sulfur removal from RFG is deeper hydrodesulfurization of refinery feedstocks. Chevron was issued a patent in 2005 for a process to desulfurize crude oil.

Federal Standards of Performance for Petroleum Refineries contained in the New Source Performance Standards (NSPS) of 40 CFR 60, Subpart J limits hydrogen sulfide (H₂S) in refinery fuel gas (RFG) burned in any combustion device to 162 ppm by volume.

The more recent Subpart Ja limits H₂S in RFG to 162 ppmv determined hourly on a 3-hr rolling-average basis and to 60 ppmv determined daily on a 365 successive calendar day rolling-average basis. An alternate requirement in Subpart Ja is 20 ppmv flue-gas SO₂ (dry) corrected to 0 % O₂ determined hourly on a 3-hr rolling-average basis, and 8 ppmv SO₂ (dry, 0 % O₂) determined daily on a 365 successive calendar day rolling-average basis.

South Coast Air Quality Management District (SCAQMD) Rule 431.1 limits sulfur compounds calculated as H₂S in natural gas to 16 ppmv and in RFG on or after May 4, 1994 to 40 ppmv averaged over 4 hours. With the advent of the RECLAIM Program in October 1993, affected facilities such as the Los Angeles area refineries did not have to comply with the command and control Rule 431.1.⁴ The 2005 baseline concentrations of total sulfur in refinery fuel gas for these refineries range from 40 to 200 ppmv. Many of them exceed the 40-ppmv allowable concentration for refinery gas in SCAQMD Rule 431.1. Equivalent sulfur oxides (SO_x) emission reductions within a given facility were apparently found elsewhere.

As a result of this study, application of the potential measures to reduce the mass of sulfur in a refinery fuel gas containing the actual pre-existing sulfur concentration results in a total sulfur concentration ranging from 11 to 102 ppmv, depending on the particular refinery. Some values still lie above 40 ppmv.

A 40-ppmv sulfur concentration in refinery fuel gas has already been justified as technologically and economically feasible in conjunction with Rule 431.1. Although Rule 431.1 itself has been subsumed by RECLAIM for the Los Angeles area refineries, that justification is still valid, and it is the recommendation of ETS that the present maximum value of 40 ppmv S in RFG be retained as the overall BARCT level.

A 40-ppmv sulfur concentration in refinery fuel gas shows up as a SO_x concentration of about 1/10 as much in the flue gas from combustion because of the nature of a hydrocarbon fuel and the combustion process. This amounts to about 5 ppm SO_x. EPA acknowledges the equivalence of 162 ppm H₂S in fuel gas and 20 ppm SO_x in the resulting flue gas (also 60 ppm H₂S and 8 ppm SO_x) in the language of the subpart Ja for refinery fuel combustion. Within round off, those ratios (162:20 and 60:8) are the same

⁴ SCAQMD Board Meeting Date November 17, 1995, Agenda #42 Public Hearing to Amend Rule Number 431.1.

as 40:5. Hence, a 5-ppm SO_x concentration in the flue gas from refinery boilers and heaters is consistent with 40 ppm sulfur in refinery fuel gas.

3. SULFUR RECOVERY UNIT/TAIL GAS TREATMENT UNIT

At the refineries' sulfur plants, large volumes of H₂S-rich gas are processed into molten sulfur, but the conversion is, of course, not perfectly efficient. Each plant is regularly reaching an approximate removal efficiency level of 99.5% or above. Still, there are technologies that can be added to the TGTU which can achieve better than 99.9% total recovery from the combined SRU/TGTU. As a consequence, ETS/AEC looked very closely at those achieved-in-practice options, in the hopes of finding some respectable SO_x reductions in those refineries not already employing state-of-the-art control technologies.

The various technologies investigated by ETS/AEC for this module and for SRU/TGTU systems are discussed below.

EXPANSION OF CLAUS PROCESSES

The Claus process was first patented by Carl Friedrich Claus in 1883. Today, Claus processes are an industry standard. There are substantial number of both 2-stage and 3-stage Claus processes in operation today.

It is common industry knowledge that, all other factors being equal, a 3-stage Claus process will yield a higher sulfur recovery than a 2-stage Claus process.

In a Claus process, H₂S is converted to Sulfur according the Claus reaction, as shown in Equations 3.1 and 3.2.



The overall reaction is shown in Equation 3.3.



The Claus process usually consists of two steps, a thermal step and a catalytic step. Though substantial amounts of elemental sulfur are created in the thermal step, the catalytic step is used to increase conversion of H₂S to elemental sulfur. This is depicted in figure 2.3 below. Claus reactions are usually equilibrium-limited. In order to

maximize the overall recovery of elemental sulfur, Claus processes are typically multi-stage operations. With each stage comes additional conversion of H_2S and SO_2 to elemental sulfur. While the first stage typically produces more elemental sulfur than any other single stage, adding stages can increase overall recovery. The amount of increase in sulfur recovery that will be realized in additional stages decreases as the number of stages is increased.

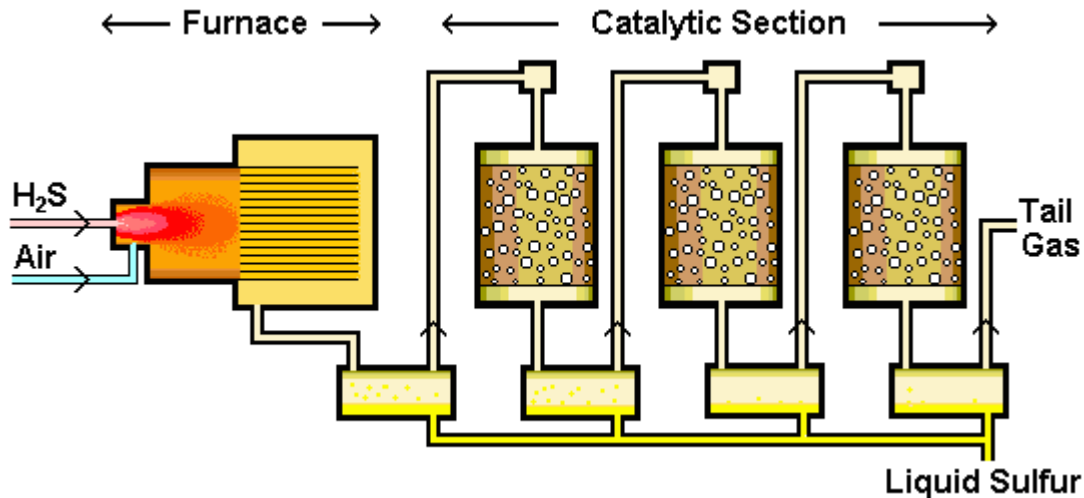


Figure 2.3: Detail of typical 3-stage Claus process taken from <http://www.nelliott.demon.co.uk/company/claus.html>

The overall SO_x reduction was determined, essentially, by accounting for the difference in removal efficiencies with respect to the current and proposed SRU/TGTU process. The SO_x emissions from the TGTU were identified/determined, using the corresponding refinery data, as the baseline SO_x available for reduction. Published and/or vendor supplied performance data for various-stage Claus units was used to determine the relative increase in sulfur removal/conversion. The downstream effects at the TGTU were not evaluated in this study and assumed to be negligible. However, it is possible that there could be some downstream impacts, so it's recommended that further study be done to confirm the magnitude of any changes.

In spite of the possible improvements to sulfur recovery by the addition of more converters, the effective present-day maximum number of stages is three. Installing more than three Claus stages is generally not cost-effective or practical. Hence, our focus on Claus units was only on SRUs currently incorporating just two such stages. The overall cost effectiveness of expanding an existing Claus SRU to include an additional (i.e., third) stage is generally and preliminarily expected to be between \$20,000 and \$30,000 per ton of SO_x reduction at a potential recovery of roughly 20 tons per year.

HYDROSULFREEN®

The HydroSulfreen process belongs to a class of SRU processes called sub-dewpoint processes. There are number of different technology providers in this area and a number of different processes, but there are a number of similarities. Lurgi's HydroSulfreen process was selected for this study. The HydroSulfreen process is an improvement on Lurgi's Sulfreen process. It adds a hydrolysis step to this process. There are over 45 Sulfreen processes in operation worldwide. In August of 2000, there were four HydroSulfreen plants licensed.

The HydroSulfreen® process is typically used for treatment of tail gas from refineries. The effluent from an existing Claus plant is first treated in a hydrolysis reactor, where species such as SO_x, CS₂, and COS are hydrolyzed to form H₂S. The effluent from the hydrolysis reactor is typically sent to the Sulfreen® process, which operates at temperatures lower than the dew point of sulfur. Operating the converters at these temperatures increases the conversion to elemental sulfur, thereby increasing the overall efficiency of the unit. Conventional Claus SRUs operate above the dew point of sulfur in an attempt to prevent the formation of elemental sulfur on the catalyst particles, which can impede the conversion process.

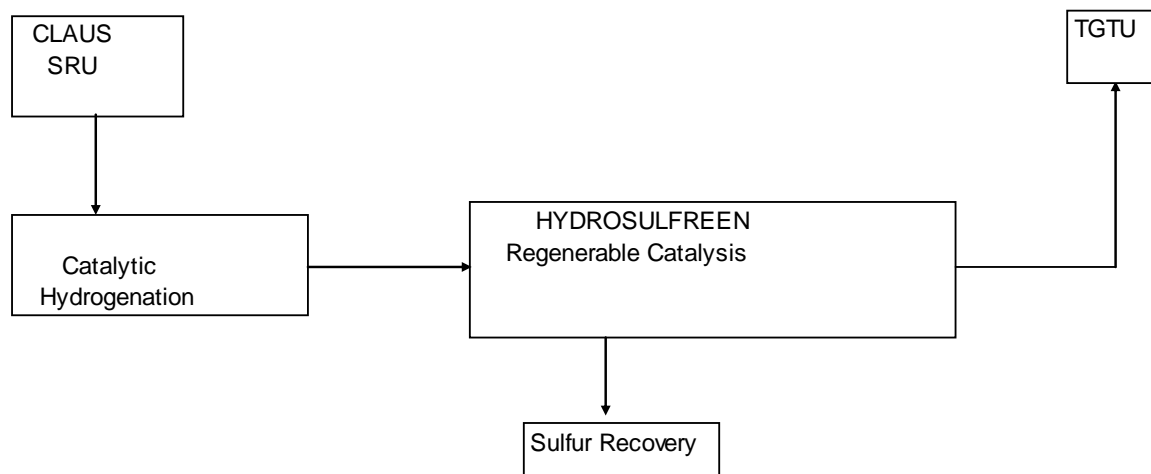


Figure 2.4: Block flow diagram of proposed HydroSulfreen addition to SRU/TGTU

Sub dew point processes, such as the HydroSulfreen® process, overcome difficulties related to sulfur deposition by using a hot gas to vaporize sulfur deposits in a regeneration cycle. One consequence of this is cyclic operation: when a converter is in the regeneration cycle, it cannot be used for conversion. Multiple Sulfreen® converters are required so that even when a converter is in regeneration, there are converters available for adsorption. As a result, operation is slightly more involved in a Sulfreen® plant than in a conventional Claus plant.

In general, the method used in determining the overall SO_x reduction for HydroSulfreen is the same as that used for the Claus expansion. Both are unit additions to the SRU/TGTU and remove an amount of sulfur from the current TGTU sulfur emissions proportional to the relative unit removal efficiencies (current vs. proposed).

The cost of installing supplemental Sulfreen® conversion on an existing Claus plant is expected to range between \$37,000 and \$600,000 per ton of reduction in SO_x emissions for most facilities. The reduction capability of Sulfreen® is generally between approximately 5 and 100 tons/year in the South Coast area refineries.

EMERACHEM SELECTIVE OXIDATION CATALYST

AQMD officials suggested that technology by EmeraChem Power LLC be evaluated as part this study. They market a selective oxidation catalyst, ES_x, that is typically used as a “sulfur trap” in conjunction with its EM_x “NO_x trap” catalyst. EmeraChem ES_x catalyst can capture multiple sulfur species, including SO₂, SO₃, and H₂S. In addition to sulfur capture, the catalyst will destroy CO, VOC, and Particulate Matter (PM₁₀). These units are typically used to treat combustion exhaust gases from incinerators, heaters, turbines and boilers.

EmeraChem does not appear to have its ES_x technology installed as a stand-alone SO_x control technology at any refinery. Their EM_x technology includes an ES_x module that removes sulfur compounds. References for treatment of exhaust gases from seven gas turbine applications have been provided to ETS/AEC. EmeraChem has provided assurances that their technology works to reduce pollution in exhaust gases across many types of unit operations, including refinery processes, gas turbines, boilers, process heaters, and diesel engines.

Here, the treating of exhaust gas from a tail gas incinerator is studied in some cases. This is depicted in figure 2.5. In others, the treating of tail gas that has not been incinerated, but, instead, has been heated to temperatures where the ES_x catalyst is active has been studied.

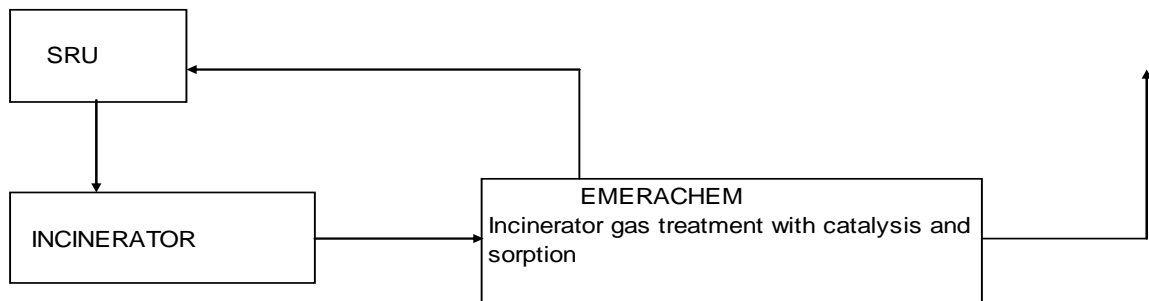
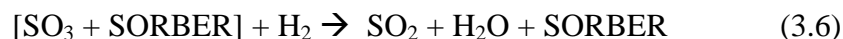


Figure 2.5: Block flow diagram of EmeraChem addition to SRU/TGTU

The ESx catalyst is a platinum group metal catalyst that stores sulfur species and simultaneously assists in the catalytic oxidation of CO and VOCs. The units are typically outfitted with multiple chambers such that exactly one chamber is always in regeneration while the other units are working to store SO_x. In the storage process, SO₂ is oxidized to SO₃ and is stored by EmeraChem's sorber.



The regeneration process releases sulfur as SO₂ according to Equation 3.6.



The cost of installing this technology in a refinery is highly variable and depends on many factors, including but not necessarily limited to the following:

1. Stack Size – Larger stacks' flows are more expensive to treat if all other factors are held constant.
2. Concentration of SO_x in the flue gas – More dilute SO_x is more expensive to remove on a per ton basis when all other factors are held constant.
3. Flue gas temperature – ESx catalyst is more efficient at higher temperatures, but has a maximum application temperature of about 1000°F. Refiners with low temperature flue gas may incur more expense on a per ton basis for SO_x removal.
4. Site specific factors – Some refineries may have characteristics and parameters that have been explored only in a very general sense at this time. Examples of possibly relevant factors include limited availability of plot space. A detailed study of the requirements at each site, specific to the installation of EmeraChem's ESx technology, is recommended before it is possible to draw conclusions regarding the cost effectiveness of this technology with high confidence.

The SO_x reductions associated with this measure were determined by, first, obtaining a vendor supplied sulfur removal efficiency and correcting it for temperature differences at the inlet of the TGTU stack. The corrected percent removal was then applied directly to the reported TGTU stack sulfur emissions to account for an emissions reduction.

ETS/AEC have completed high-level cost estimates for the installation of the ESx technology at several of the refineries under the jurisdiction of the SCAQMD. It has

been estimated that the cost per ton of SO_x reduction using EmeraChem's technology falls in an approximate range of \$10,000 – \$60,000. The potential for SO_x reduction falls in a rough range from 14 to 60 tons/year.

SULFUR PIT VAPOR CAPTURE

This is not a technology *per se*, rather it is a point of treatment. Several different technologies can be implemented within the scope of this concept. However, many refineries worldwide employ some kind of sulfur pit vapor capture and treatment. A detailed discussion by Mahin Rameshni of Worley Parsons entitled "Options for Handling Vent Gases in Sulfur Plants" addresses many of the most practical potential implementations of this measure.

The concept behind our suggested implementation of this measure is to capture, rather than incinerate and release, vapor that normally is pushed out of the sulfur pits. A general detail of this measure is depicted in figure 2.6. Once captured, the sulfur vapors can be returned to the SRU/TGTU treatment train. In some cases, there already exists a mechanism to return sulfur vapors to the treatment train, but improvements may be possible. The scope of such projects can vary greatly because there are several site-specific factors and processing details that dictate the level of effort required to retrofit a sulfur plant with control technology. In addition, the benefit that can be expected from such efforts is highly site dependent. Nonetheless, there is some potential to reduce emissions by improving the capture and conversion of sulfur species at the sulfur pits.

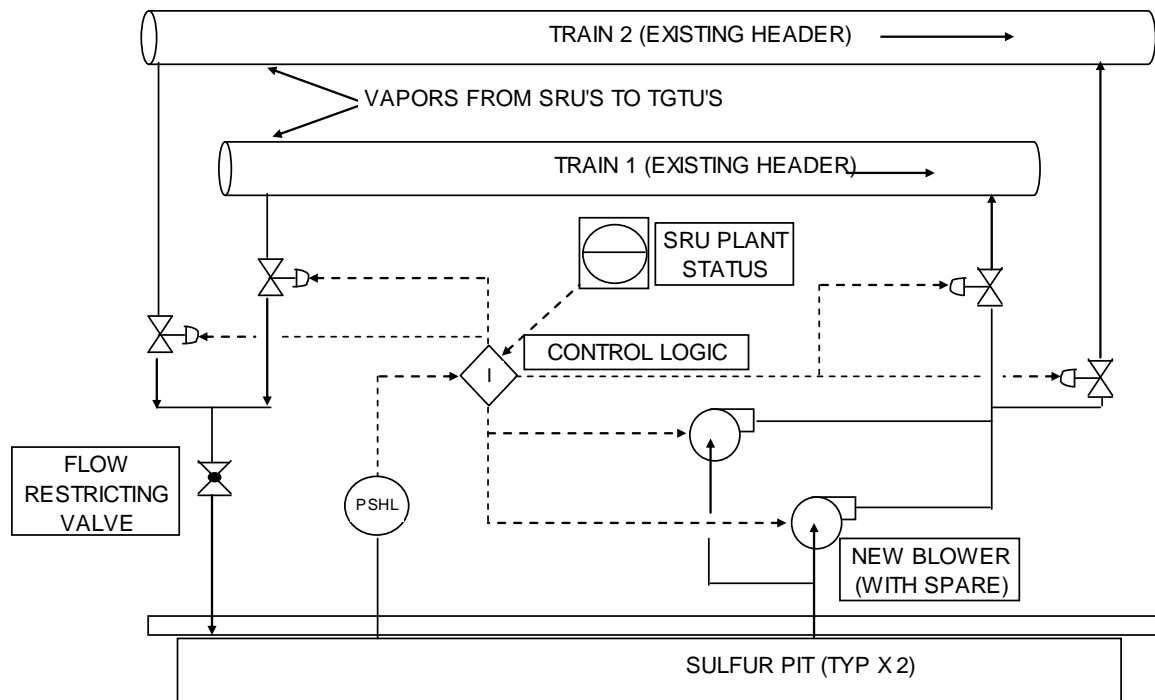


Figure 2.6: Generic detail of a design for recycling sulfur pit vapors

In general, the overall SO_x reduction for this measure was determined by, first, estimating the amount of SO_x emissions attributed to sulfur pit vapors. Since the sulfur pit vapors are sent to the TGTU, published and/or vendor supplied sulfur removal efficiencies for the corresponding TGTU were used to determine the overall SO_x reduction.

ETS/AEC have estimated that the cost of capturing vapor from sulfur pits (where, that is, it is not already constantly or regularly processed through the SRU/TGTU) and returning it to the SRU/TGTU is expected to fall in an approximate range of \$4,000 to \$17,000 per ton of emission reduction. The reduction in emissions is generally between 20 and 50 tons/year.

ADDITION OF TG-10 TO AMINE SYSTEMS

In some cases, TG-10 can be added to tail gas treating amine systems. TG-10 is a proprietary amine mixture offered by INEOS Gas/Spec. It has been designed to be highly selective for H₂S. INEOS Gas/Spec has published data, comparing the capabilities of TG-10 and MDEA in actual tail gas plants. The details of TG-10 additions in amine systems for tail gas treating are similar to those for TG-10 additions to fuel gas treating systems. For many reasons similar to those in fuel gas treating, the effectiveness ratios for TG-10 can appear to be quite attractive. The cost effectiveness ratios for TG-10 additions in tail gas treating amine systems have been estimated to be between \$2000 and \$3000 per ton of emission reduction. The capacity for emission reduction per installation has been estimated to fall in an approximate range of 15 – 25 tons per year. Any definitive conclusions regarding the costs or capabilities of amine additives are premature at this stage. It's unlikely, but there may be modifications to the refinery required to support slightly different amine recirculation rates, heat duties, equipment metallurgy, tower internals, or other changes that have not yet been identified. Also, the emission reduction capacity has only been estimated, though one refinery performed some limited testing and confirmed the results at the very end of the project. A detailed study and possibly the collection and analysis of data not currently available to the refineries may be required to confirm the above estimates, if this measure were ever to be implemented.

GENERAL DISCUSSION & CONCLUSION

The Sulfur Recovery Units (SRUs) and Tail Gas Treatment Units (TGTUs) in modern refineries are highly efficient processes, capable of rapidly removing almost all of the sulfur in their feed streams. Despite their efficiencies, the SRU/TGTUs in today's refineries are often significant emission sources for SO_x, relative to other units in

refineries. For this reason, the SRU/TGTU is a good candidate for the study of retrofit control technology installation.

Based on the cases examined in this module, performance of the technologies to control SOx emissions from the SRU/TGTU in the SCAQMD area refineries ranges from under 5 to over 100 tons per year.

Of all the technologies studied, the least costly emission reduction technology on a per ton basis is the addition of TG-10 additive to existing amine systems. This is only feasible for refiners that have amine systems that can accept an addition of TG-10.

Other technologies studied include the expansion of existing Claus operations by adding more stages, capture of vapors from sulfur pits, installation of a HydroSulfreen® process, and EmeraChem's ESx system. Each of these technologies shows the potential for emission reductions at a fairly expensive cost per ton. However, they do appear to be feasible and can provide reductions in SOx emissions of at least 50 tons per year in some refineries.

According to our analysis, most emission reduction technologies in the SRU/TGTU will come at a cost in excess of \$10,000 per ton. There may be a relatively small number of opportunities to decrease SOx emissions from the SRU/TGTU by as little as \$3000 per ton. There is no universal solution or technology that is most suitable for reducing SRU/TGTU emissions at all refineries. Wide variations in both the cost per unit mass emission reduction and the capability of technologies to reduce emissions have been observed across different operations.

The following table summarizes the study results from both Module 2 and 3A, including the identification of the recommended treatment measures chosen for the refineries' SRU/TGTU systems:

<u>Treatment Method</u>	<u>Annual SOx Reduction (tons/year)</u>	<u>Capital Cost (\$MM)</u>	<u>Cost Effectiveness (\$/ton SOx)</u>
Catalytic treater	53.0	\$12.7	\$12,881
Wet scrubbing	61.4	\$37.8	\$39,000
Catalytic treater	13.7	\$10.5	\$54,686
Wet scrubbing	20.8	\$39.4	\$123,186
Wet scrubbing	106.3	\$51.3	\$36,359
Catalytic treater	<u>46.8</u>	<u>\$12.6</u>	<u>\$22,410</u>
	301.9	\$164.3	\$37,412

Assuming that the refineries would implement all the commercially available treatment measures (both modules 2 and 3A) recommended by ETS/AEC, the overall emission reductions from SRUs/TGTUs would be 301.9 tons per year (0.83 tons per day) at an average cost effectiveness of \$37,412 per ton SO_x reduced (within -10% +50%).

4. ETS RECOMMENDATION FOR SULFUR RECOVERY UNIT/TAIL GAS TREATMENT UNIT

SRU / TGTU

Subpart J (Standards of Performance for Petroleum Refineries) in the New Source Performance Standards (NSPS) of 40 CFR 60 contains provisions for refinery sulfur plants. For a Claus sulfur recovery unit followed by incineration, the standard is 250 ppmv (dry) at 0 % O₂. For a system not followed by incineration and vented directly to the atmosphere, it is 10 ppmv of hydrogen sulfide (H₂S) and 300 ppmv (1.2 x 250) of reduced sulfur compounds, each calculated as ppmv of SO₂ (dry) at 0 % O₂. The term *reduced sulfur compounds* is defined as hydrogen sulfide (H₂S), carbonyl sulfide (COS), and carbon disulfide (CS₂).

Subpart Ja states the same limits for a sulfur recovery plant with a capacity greater than 20 long tons per day (LTD) of sulfur product. It adds that a sulfur recovery plant consisting of multiple trains or multiple release points shall comply with the same SO₂ limit for each process train or release point or as a flowrate-weighted average for all release points. Smaller sulfur recovery plants with capacity of 20 LTD or less are allowed to emit at 10 times the above limits. The term *reduced sulfur compounds* has the same meaning as in Subpart J.

Formulas are provided in Subpart Ja to calculate the allowable emission rate of SO₂ for Claus plants employing oxygen enrichment. These formulas reduce to the above limits when using 20.9 % O₂ (atmospheric air). In the extreme of 100 % O₂ fed to the Claus plant, they calculate to 800 ppmv and 8,000 ppmv SO₂ (dry), respectively, for large and small sulfur plants. The reduced sulfur compound limits at 100 % O₂ are 1.2 times the SO₂ limits; that is, 960 and 9,600 ppmv calculated as SO₂ (dry).

Except for one refinery, whose SRU tail gas is regularly vented, and another refinery whose combustion device is considered by the refinery not to be a treatment / control device of the tail gas unit, the 2005-baseline SO_x in the SRU is about 100 ppmv (@ 0% O₂) or less. These figures are well below the 40 CFR 60 Subpart J (or Ja) standard of 250 ppmv SO_x (@ 0% O₂).

Guaranteed outlet SO_x concentrations of 5 ppmv after scrubbing can be achieved, in the worst case at 95% SO_x removal efficiency; in most cases, the required scrubbing efficiency for a 5-ppmv SO_x outlet is considerably less. Belco has demonstrated experience in scrubbing the SO_x from incinerated sulfur plant tail gas as well.

Except for the two aforementioned refineries, it has been found possible in this study also to reduce SRU ppm SO_x to the atmosphere by the gas treating techniques investigated. Those results are all below 10 ppmv, and in many cases below 5 ppmv.

The ETS recommendations for SRU / TGTU emissions are therefore as follows:

- For uncombusted tail gas, the limits of Subpart J (Ja), namely 10 ppm H₂S and 300 ppm reduced sulfur species (total of H₂S, COS, and CS₂), should continue to apply. Refineries should be encouraged to reduce emissions so as to be able to vent rather than having to combust SRU / TGTU tail gas.
- For combusted / incinerated tail gas, 5 ppmv SO_x @ 0% O₂ should be defined as the overall BARCT for all refineries, based on scrubbed flue gas, but permissible to achieve by whatever means possible. A level of 10 ppmv would allow a greater number of refineries to meet the overall BARCT level by the gas treatment methods of Module 2 without having to install a wet gas scrubber (Module 3A).

IV. COST ANALYSIS

A. APPROACH & BASIS FOR COST ESTIMATE

A Discounted Cash Flow (DCF) cost analysis was performed for each selected application. The DCF approach determines the value of a project using the time value of money by estimating all future cash flows and discounting them to determine the equivalent present value cost. For consistency with other AQMD rule development projects and Air Quality Management Plan (AQMP), present value (or present worth value, PWV) was estimated with the following equation:

$$PWV = C + (CF_1 \times A) - (CF_1 \times S) + \text{SUM } (CF_{2,n} \times F_n)$$

Where:

C = Capital cost, \$, a single payment

A = Annual cost, \$/yr, a series of uniform payments

S = Annual savings, \$/yr, a series of uniform negative payments

F = Future cost, \$, a single payment in a future year

CF_1 = Conversion factor from compound interest tables of the formula

$[(1 + i)^n - 1]/[i \times (1 + i)^n]$ where i = fractional interest rate and n = the n th year from the beginning. Used with a series of uniform payments from 1 to n .

$CF_{2,n}$ = Conversion factor from compound interest tables of the formula $1/(1 + i)^n$. Used with a single payment at any year n .

To be consistent with AQMD cost-effectiveness analysis, a 4% annual interest rate was used in the calculations.

The DCF includes all anticipated capital and expense costs associated with the project or measure being evaluated. The capital portion of those costs includes materials, labor, and other directs, as well as engineering, management, taxes, shipping, and various indirect costs incurred for the particular control technology. (Note that the team attempted to estimate and include in the cost estimates all the monies required to construct and/or supply utilities (such as steam, electricity, and water), as well as infrastructure (e.g., sewer and wastewater treatment), associated with each measure.) Every cost item to be incorporated in the estimate is site and equipment specific. And, wherever possible, cost elements were individually listed, quantified, and costed via the use of applicable unit rates. In that fashion (i.e., “line-item” estimating, in lieu of purely factored costs), the relative precision of the overall estimate has been optimized. What’s more, reviewers of the cost development sheets will have the greatest insights into how the estimates were assembled; they will therefore be able to more easily adjust the results to reflect scope changes or improved data in the future.

Whenever possible, vendor/manufacturer budgetary quotes and local material/labor costs were used in our estimates. But when they were not available, ETS/AEC’s standard cost estimating methodologies for material and labor—all particular to refineries—were used to complete the pricing exercises.

B. APPROACH & BASIS FOR EQUIPMENT SIZING

The methodology and techniques utilized during this project in the sizing of equipment for a new application (e.g., for a sulfur treatment package) are exactly those used in any engineering endeavor. First, of course, we obtained a full understanding of how the

existing system is configured and operates; those things are known by means of the site visit, underlying industry knowledge, interviews of refinery personnel, refinery-submitted data and drawings, etc. The second step was to conceptualize how the equipment under consideration is/are to be installed. This also includes identifying the performance parameters to be achieved. In doing so, we quantified the expected ranges of service and efficiency, so that an appropriate over-design allowance could be applied (the purpose of which is to ensure that the performance objectives will reliably be met even if the underlying process is running at one extreme or another of its normal range). Next, all the pertinent information was communicated to the equipment representative, usually for pricing determination, but sometimes also to confirm the sizing exercise. In all cases, evaluating specific technology options required eventual coordination with the manufacturer or licensor to get verification of critical assumptions and/or conclusions.

Since the study encompassed multiple facilities and systems with widely different process flows and arrangements, and because, furthermore, there were several optional technologies looked at for each installation, the total collection of potential measures was extraordinarily large. Thus, it was impossible—in the short timeframe available—to address every one of the individual cases with a full set of vendor inquiries. Instead, the team made use of generic, but representative budgetary quotations and published cost studies for the various technologies. Each such “reference point” (i.e., package cost and performance data for a prescribed process operating condition) was then used as a basis for extrapolation to other locations and design conditions. For a specific application, the key sizing criterion (typically the process throughput—e.g., scfm of fuel gas) is determined or calculated from the relevant operational data. Then, to generate the probable capital purchase cost (\$PC), that criterion value (V) is divided by the comparable numerical capacity (Cr) from the “reference point” package. Using the baseline capital cost (\$BCr) for that “reference point”, the desired capital cost is mathematically calculated via a conventional power curve relationship:

$$\text{\$PC} = \text{\$BCr} \times (\text{V/Cr})^n$$

where n is an appropriate exponent between .5 and 1.0

This approach is commonly used in engineering studies, and has been widely described in reference books such as Marks Handbook and Perry's Handbook of Chemical Engineering. For our studies, the exponent value, n, was normally assigned a value between 0.6 and 0.7, a range that historically has given good estimates for industrial equipment packages.

Insofar as the pertinent sizing criteria were concerned, they were compared to nameplate duties for other, similar units for rough verification purposes. Also, input was sought directly from the manufacturers' representatives, as well as public domain literature and published case studies. In the end, the checking procedures employed by the team members helped us to achieve rough, budgetary purchase costs, knowing that any loss in precision in arriving at those costs would be adequately covered by the very broad overall cost ranges (i.e., +/- 40%) expected for the ultimate results.

C. EQUIPMENT COST INFORMATION

ETS/AEC worked as closely as possible with the technology suppliers to gather the direct capital cost estimates for this project. (Where available, too, we compiled net installation costs which had been reported by the manufacturers for "reference points", as described in the preceding section. Those "turn-key" costs were used to check the built-up cost estimates assembled by the project team.) Also, we took advantage of our relevant and extensive corporate knowledge base for similar projects. Every valid method was employed to give the best possible output. (In addition, as mentioned in Section A, above, indirect costs for impacts to utilities and infrastructure were estimated and included.)

The following list summarizes how the team typically pulled together a complete capital cost estimate for a given measure:

<u>Cost category</u>	<u>Cost determination method(s)</u>
Primary technology package	Obtain budgetary quote from vendor or use the aforementioned "power factor" equation for an extrapolated value. The study tried to distinguish where the Primary technology package is provided as a skid type package unit, loose as major components, or only as a process design and specification. Based on these different assumptions, hours for Engineering, Procurement, and Construction (EPC) contractors to design the balance of the package, procure remaining material, manage the project and construction, and construct the complete package have been included in the estimate. This cost also includes any equipment and material that is not part of the main vendor's supply.

Discipline-specific commodities	<p>Use approximate takeoffs and multiply them by historically confirmed unit rates, when possible; otherwise, employ suitable allowances.</p> <p>Approximate takeoffs have been developed by considering that material that might be supplied as part of a Primary technology package and that such portions of the materials might be designed, supplied and installed by an EPC contractor.</p> <p>Because of the preliminary nature of the layouts and designs, robust allowances for potentially greater material quantities in the final designs have been utilized when appropriate.</p>
Construction labor	<p>Use standard industry-specific unit labor rates for all the commodity items referred to above, and then compute the product of quantity times unit rate times basic refinery-specific hourly labor rate (the latter determined by laborer classification)</p>
Indirect/overhead costs	<p>Apply appropriate percentage factors against either sub-total labor or material costs</p>
Engineering/management	<p>Estimate specific manhour totals based on design experience in the industry and knowledge of the process and refinery-specific aspects of the measure</p>
Project contingency	<p>Choose an appropriate percentage to apply against the bottom-line capital cost estimate (the contingency used reflects the degree of uncertainty on the total package, and normally is between 25% and 40%, inclusive)</p>

Owing to the fact that all the cost estimating tasks were conducted in a very preliminary, conceptual fashion, the overall accuracy of the capital cost determinations is no better than +/- 40%. Considerable engineering study would be required to refine the cost estimates and arrive at narrower accuracy ranges.

We are well aware of the multiple phases that projects of this magnitude go through, particularly in petrochemical plants and refineries, prior to receiving full funding and authorization to proceed into detailed design. Often a full front end engineering design (FEED) package is developed, which for many companies requires up to a 60% design effort and a $\pm 20\%$ cost estimate. But because of very real constraints on this project (such as time, budget, and minimum breadth of analysis), we did not have the luxury of developing a fully detailed engineering package for any SO_x reducing measure. Instead,

each estimate served as the best possible first pass amount for use in the DCF analysis mentioned above.

D. ANNUAL OPERATING COSTS

As part of our initial pre-visit questionnaire, we asked each refinery to provide us with the actual, current costs for various utilities and infrastructure services. Also, while on-site we requested typical plant hourly rates for outside skilled labor trades constructing new projects. All this information was loaded into our refinery-specific cost estimating spreadsheets.

Unit rates for the principal cost-incurring utilities were requested from the refineries at the outset of the study. In several cases, explicit values were provided in response to the requests; those values were used as advised us. For all other instances, generic estimates—obtained from other work by AEC at various U.S. refineries—of the unit rates were utilized. Of course, the explicit rate structures were refinery-specific, but the table below shows the ranges by commodity applied in the six individual reports:

<u>Utility/Infrastructure</u>	<u>Unit of measure</u>	<u>Min. cost/unit</u>	<u>Max. cost/unit</u>
Natural gas	MM BTU	\$6.92	\$10.13
Electricity	kw-hour	\$0.05	\$0.108
Fresh water	MM gallons	\$2449	\$4120
Wastewater treatment	MM gallons	\$600	\$6000
Cooling water	MM BTU	\$0.50	\$0.50
Compressed air	1000 scf	\$0.15	\$0.25
Solid waste disposal	ton	\$100	\$100
Sulfur*	Long ton	\$35	\$400

*--this commodity is a by-product of refining, and therefore provided revenue, not cost

Likewise, AEC had requested from the refineries the average hourly costs for various labor classifications on typical capital projects. When plant-specific values were not provided, we used generic labor rates that are intended to reflect average fully-burdened costs for jobs inside a South Coast refinery. The value ranges are shown below:

<u>Labor Classification</u>	<u>Lowest hourly labor rate</u>	<u>Maximum hourly labor rate</u>
Laborer	\$90	\$106
Civil/Concrete Worker	\$90	\$106
Structural/Iron Worker	\$95	\$113
Painter	\$90	\$106
Insulator	\$100	\$106

Mechanical/Machinist	\$105	\$108
Boilermaker	\$106	\$115
Pipefitter	\$95	\$109
Electrical/Electrician	\$106	\$113
Instrumentation Tech	\$106	\$113

The majority of the suggested control technologies or upgrades include the need not only for additional utilities but also raw materials, such as a scrubbing agent or catalyst. Costs for those items were estimated through consultation with a technology supplier or in-house expert. The appropriate third party resource or corporate engineer(s) based the quantity determinations on the specific characteristics of the technology under study. Once a quantity was determined, a local material cost was obtained for use in the calculations. Moreover, costs that recur at multiple-year intervals, rather than annually (e.g., those incurred during turnarounds or periodic major maintenance activities), have been accommodated in the project's workbooks.

The worksheets into which all the aforementioned information has been entered make automatic calculations of annual operating costs. They permit the easy adjustment of parameters, such as utility rates and labor demands, in case updated values are later made available. The final programmed calculation is the one that finds the PWV (Present Worth Value) of each measure's multi-year cash-flow. That value is computed using the same 4% discount factor mentioned above. It represents, in 2008 dollars, the single lump-sum expenditure that is equivalent—in financial terms—to the said cash-flow distribution.

Annual usage of solvents and utility (e.g. natural gas, electricity) usages are summarized in the confidential appendix of each refinery for the specific treatment measures selected.

E. COST EFFECTIVENESS ANALYSIS

The cost effectiveness, **CE** (\$/ton SO_x reduced), of a prospective technology installation for this study is defined as the ratio:

$$\mathbf{CE} = \mathbf{PWV} / (\mathbf{25} \times \mathbf{SR})$$

where **PWV** is the *Present Worth Value* (units: \$),
SR is the *annual reduction in SO_x emissions* (units: tons per year), and
25 is the economic life (in years) of the measure

In computing for a particular measure (at a specific refinery) the expected annual reduction in SO_x emissions (the term “SR”, above), the AEC team first determined the baseline emissions for the equipment or system. Those emission amounts are the ones that the refinery either measured or calculated, and then reported to the AQMD, all in accordance with the accepted protocols for major source reporting. When data from that year was available, the baseline amount was for the full 2005 fiscal year; otherwise, the quantity as reported from the next or a subsequent year was selected.

Next, the candidate technology or approach was evaluated in light of the equipment’s or system’s operating characteristics. This was done to arrive at either (a) a directly computed net mass for the expected annual SO_x reduction, or (b) the expected percentage reduction in SO_x emissions, by implementing the measure. In either case, the outcome is a predicted reduction, in tons/year, of total SO_x emissions; that is the parameter “SR”. (The SO_x emissions reductions, in general, are always in agreement with published data and/or marketing/sales data for the respective technology or system.)

In a parallel effort, and as defined in a previous section, the “PWV” for the measure was computed. Certain underlying assumptions were utilized in that calculation. Those primary assumptions are shown in Table 4.1 below:

Table 4.1: List of Assumptions for Cost Analysis

The following list provides assumptions/information used in the cost analyses for refinery controls. These assumptions are generalized to cover the several types of controls and process equipment analyzed. Many of the following assumptions need to be refined once more detailed study, under separate contracts, of selected measures is undertaken.

- Costing is for scrubbers, though not evaluated in Module 2, of one type or another at each site and for each process to be controlled. Scrubber equipment cost is based on one or more quotes or cost studies for known sizes of each type of scrubber. AEC estimated major equipment costs for each of the refinery processes to be analyzed by using “the six tenths power factor” rule applied to vendor information as described in Section IV B of this report.
- Especially for large projects, significant front-end engineering design (FEED) and project management costs are incurred (thousand or tens of thousands of hours for FEED and thousands of hours for management). It should be noted that the number of engineering hours chosen for arriving at the project costs is an assumption. These hours are based upon AEC’s first-hand experience as well as reported refinery experience.¹
- For all projects, representative contingency allowances, based on the nature of the project, have been made.²
- For all projects, a fixed design development allowance of 10% has been stipulated.²

- The baseline emissions for each plant's processes are supplied by SCAQMD or the refineries.
- Scrubber control efficiencies are based on vendor estimates for similar processes.
- Life of control equipment is 25 years after startup in all cases.
- An annual discount rate of 4 percent is used and all costs are in 2008 dollars.
- Purchased equipment costs for the scrubbers are estimated with auxiliaries, instruments, freight, and taxes.
- Costs include site preparation and construction based on the footprint of the control equipment. (It should be noted that when installing equipment in an existing refinery, the vendor's proposed footprint may not be accurate as the equipment may need to be separated to fit in the existing area and some equipment may be located off-site for space or operating considerations. Therefore "robust" material take off allowances are justified to deal with this spread out footprint.)
- Installation costs include labor and materials.
- Added charges for seismic considerations (Zone 4) are included in equipment costs.
- Added charges for waste or wastewater treatment equipment are included in equipment costs unless treatment is performed outside of the boundary limits for the control measure. In these cases, the treatment costs have been calculated according to the treatment requirements and site-specific unit costs provided by the refineries.
- Annual operating/maintenance costs are estimated from equipment and labor costs at rates obtained from the refineries or from rates for similar workers at other refineries. The fully burdened rates are from \$90 to \$113 per hour and are listed by labor classification in Section IV D of this report.
- Overhaul (turnaround) maintenance is performed every 5 years starting the fifth year after startup
- Startup may be 1 to 3 years after the project begins, but all capital cost for the equipment and installation is spent in the first year. Capital required for installation is expected to be larger in years after the first and is apportioned likewise. (There are, however, exceptions to the preceding. The details depend on the length of delivery and schedule of construction. Some equipment might have a delivery of one year or more and construction cost will not occur until the unit is delivered and installed, which will be beyond one year. Cost might be "committed" in the year but not "expended" until the invoices are actually paid, so the timing of costs becomes a project-specific question. Also, note that a major project start-up might not be until 5 years after the project is initiated in Front-End development.)
- Utility rates in \$/unit during construction and operation are as reported by the refineries under study, or if not available, from similar refineries elsewhere. Ranges of costs for the various utilities are given in Section IV D of this report.
- Accuracy of the costing is estimated by AEC at no better than +/- 40 percent and of the subsequent cost effectiveness at -10 to +50 percent.

Footnotes:

1) Estimated Engineering Hours:

ETS decided to test the AEC assumption by contacting three parties with significant experience in estimating and implementing the installation of air pollution systems, in particular SO_x scrubbers. All three were asked to estimate the number of engineering hours required to specify, design and install a 100,000 to 200,000 ACFM wet scrubber system for SO_x removal at a California refinery.

The first of these estimates was obtained from an executive of a relatively small firm that provides turnkey systems. This executive has a wealth of hands-on experience in the design and supply of air pollution control projects. His estimate of 6,000 to 9,000 engineering hours was based on a recently completed contract. Included in his estimate was an adjustment (increase in hours) to accommodate anticipated demands and complexity of a refinery project.

The second estimate was from a well-respected engineering manager at a relatively large Midwest engineering firm. His estimate was between 20,000 and 30,000 engineering hours.

The third estimate was a utility firm project manager who had recently completed a retrofit of a very large multi-unit and baghouse system for control of coal-fired boiler SO_x and particulate emissions. He stated that "if the engineering scope includes foundations, electric power, ductwork connections, access, elevators, fly ash system, flow modeling, P&ID's, etc, he would think the work could require at least 10,000 man hours (5 man-years), and quite possibly closer to the 30,000 man-hour estimate".

Based on the above ETS believes that the engineering hours used in the cost estimations in this report are conservative and given the softening in the economy it is possible that the actual hours could come in below those used here.

It should also be noted that engineering hours are separated into two categories, front-end engineering and design (FEED) hours, and a design allowance taken as a percentage of total materials, labor, and overheads required to complete a project. This latter percentage is not part of, for example, the 30,000-hour estimate given above.

2) Contingencies:

In Module 2 ETS/AEC has assigned 10% for design allowance and 25%-40% for contingency. The following contingencies were applied by measure in Module 2:

M10, M11: 40%

M4, M20, M21: 35%

M14, M15: 30%

M16, M22: 25%

It should be noted that the EPA Air Pollution Control Cost Manual, 6th edition, lists contingency percentages for most of its control systems as 3% of purchased equipment cost (PEC). PEC consists of equipment and auxiliaries, instrumentation, sales taxes, and shipping.

The spreadsheets for estimating PWV are adapted from a procedure that estimates net present value on a line-by-line (year-by-year) basis beginning a specified number of years before startup (1 to 4). Capital costs for equipment purchase and construction are included in the years preceding startup. This procedure estimates net present values that are different from AQMD's PWV.

Because of this difference the spreadsheets have modifications that use the line-item costs, but regroup them in a manner suitable for use in the PWV equation.

- Categorized costs include:
 - Demolition and decommissioning
 - Civil/concrete
 - Structure
 - Equipment
 - Piping and Mechanical
 - Electrical and controls
- Miscellaneous line items include:
 - Contractor overhead, typically 8 % of direct field labor (DFL)
 - Contractor field supervision, typically 12 % of DFL
 - Mobilization/demobilization, typically 10 % of DFL
 - Overtime/productivity factor, typically 12 % of DFL
 - Freight and shipping, typically 8 %, of materials
 - Sales tax, typically 7 % of materials
 - Commissioning and operating spares, typically 5 % of materials
 - Startup/initial fill material, typically 2 % of materials
 - On-site training/startup assistance, depends on project
 - Front-end engineering design, depends on project size
 - Project management, depends on project size
 - Design development allowance, 10% of total
 - Contingency, 25-40% applied against the bottom-line capital cost estimate

F. TOP-DOWN APPROACH

Selection Process for Recommended Emission Reduction Measures

For the refinery operations discussed in this report the following sections show how emission reductions were estimated and how recommended treatment measures were selected. Initial operations and emission points for study were chosen from questionnaire responses and visits to the refineries. These choices were then analyzed and compared

from data supplied by the individual refineries and from equipment vendors. Spreadsheet models were used to develop SO₂ quantities before and after control equipment, then to estimate costs of control and cost effectiveness. The top-down approach followed here consists of identifying sources expected to be the higher emitters, then analyzing performance and cost, first of the expected most effective control systems, then the second most effective system. Detailed calculations for sulfur into and out of each control system are shown in tables provided in the Module 2 confidential appendix for each refinery, but example calculations are given below.

Fuel Gas Treatment

Refinery fuel gas (RFG) is typically a mixture of gases generated from sources such as fluid catalytic crackers, cokers, hydrotreaters, and crude oil separations. Gas from the individual sources may be routed to a mixing vessel, then to a manifold system for distribution to a variety of heaters, boilers, furnaces or other combustion sources scattered about the plant. As described elsewhere in this report, the individual gas streams may have sulfur-compound compositions that are significantly different from each other. Sulfur-compound removal by solvent absorption is most effective when the solvent, or mixture of solvents, is tailored to the gas stream's composition.

Sulfur compounds can be removed at different points in the RFG routing: from each source of generation, from the outlet side of the mixing vessel, from the inlet side of each combustor, or from the outlet of each combustor. All points but the last have a mixture of sulfur compounds, while the combustor outlets contain primarily SO₂ that can be removed by chemical scrubbers. Also, downstream process sulfur removal capabilities must be considered to ensure that reductions from evaluated measures do not take credit for sulfur removal already occurring at the facility.

All other things being equal, economies of scale might suggest that a solvent absorber at the outlet to the mixing vessel is the most cost-effective measure for removing sulfur. However, not all other things are equal. Individual RFG streams have varying flow volumes and concentrations; one stream may be so large as to make the other streams nearly insignificant. For that case a solvent absorber on the one stream might be more effective than treating the mixture of all streams. Similarly, one or two combustion sources might be so large as to make the others insignificant. If highly efficient control is obtained at the mixing vessel, further treatment at the combustors is likely not to reduce sulfur oxides significantly or to be cost effective. As shown in the Module 3A report, this latter situation leads to having no selection of emission reduction measures on heaters and boilers.

Results of estimating effective SO_x reduction and associated cost for RFG controls are shown in Appendix A, Table A-2, which summarizes the selected measures

recommended by the study team. That table shows no results for measures not recommended, nor does it explain why different measures were chosen for different refineries. The following text explains the selection process and shows how the emission reductions were estimated.

Tables provided in the refinery-specific confidential appendices for Module 2 show the measures examined for RFG at each refinery. Estimated installed equipment cost, cost effectiveness, inlet and outlet SO₂ concentrations, control efficiency, emission reductions, treatment measure recommendations, and notes are shown for each case. Because these tables may contain company-sensitive information, they appear only in the confidential appendices for Module 2 supplied to each refinery and to SCAQMD. However, an example case with artificial data is given below.

Assume the plant questionnaire shows a set of absorbers associated with the RFG system that emit significant amounts of SO₂. These absorbers are discussed with plant personnel and it appears that one set could convert its amine system to a Sulfinol system at relatively low cost. The Sulfinol is expected to absorb more of the non-H₂S sulfur compounds in the RFG than does the current amine solvent, assuming no additional downstream process removes that same sulfur today. To estimate the available SO₂ reduction, gas flow rates and sulfur quantities in the gas are required. Plant information shows a flow rate of 450,000 scfh, which when multiplied by 24 gives a daily flow rate of 10.8 million scfd. Further information shows that the current absorbers have inlet concentrations of 85 ppmv for the H₂S portion and 155 ppmv for non-H₂S sulfur compounds. Corresponding outlet concentrations are 9.35 ppmv and 82.8 ppmv. Inlet mass rate of SO₂ is found from:

$$10.8\text{E}6 \text{ scfd} \times (85 \text{ ppmv} + 155 \text{ ppmv}) \times 64 \text{ lb SO}_2 / \text{lb mol SO}_2 / (379.5 \text{ ft}^3/\text{lb mol} \times 2,000 \text{ lb/ton}) = 0.084 \text{ tpd to absorbers,}$$

where the value 64 is the molecular weight of SO₂, which with the one-to-one mol correspondence of sulfur converted to sulfur dioxide can be used directly to obtain mass of SO₂.

Vendor information shows an expected efficiency for the non- H₂S species of 97 percent down to a lower limit of about 5 ppmv.

Outlet concentration of the non-H₂S compounds removed with Sulfinol is found from:

$(1 - 0.97) \times 155 = 4.65 \text{ ppmv}$. This value is less than 5 ppmv, so 5 ppmv will be used as the outlet concentration for non-H₂S compounds. The mass rate of SO₂ from the Sulfinol absorber is found from:

$$10.8\text{E}6 \times (9.35 \text{ ppmv} + 5 \text{ ppmv}) \times 64 / (379.5 \times 2,000) = 0.013 \text{ tpd}$$

SO₂ removed is $(0.084 - 0.013) = 0.071$ tpd, or when multiplied by 365 days/yr,
= 25.86 tpy.

With a present worth value of \$8.24 million and equipment life of 25 years, cost effectiveness is:

$$\$8.24 \text{ million} / (25.86 \text{ tpy} \times 25 \text{ yr}) = \$12,700/\text{ton}.$$

At the coker off-gas location a Merox system can be installed for SO₂ removal. The flow rate at this location is 6,307.2 MM scf/year with an average sulfur content of 85 ppmv. Non-H₂S sulfur compounds are about 90 percent of the total. Total mass of SO₂ to be treated is:

$$0.9 \times 85/1 \text{ million} \times 6,307.2 \text{ MMscf/year} \times 64 \text{ lb/lb mol} / (379.5) / 2,000 \text{ lb/ton} = 40.7 \text{ tpy}$$

The Merox vendor claims 91 percent removal efficiency of Merox for the coker gas, thus SO₂ removed is $40.7 \times 0.91 = 37.0$ tpy

With a present worth value of \$43.0 million and life of 25 years, cost effectiveness is:

$$\$43.0 \text{ million} / (37.0 \text{ tpy} \times 25 \text{ yr}) = \$46,500/\text{ton}$$

Appendix A, Table A-3 shows the results of the example case and gives a recommendation of the selected treatment measure. The table shows the two measures chosen for costing: M20 uses Sulfinol as a replacement solvent for existing amine in absorbers controlling fuel gas, and M21 adds Merox treatment to the coker off-gas. In this case Sulfinol removes somewhat less SO₂ but is nearly a quarter of the cost. The recommended choice is the Sulfinol replacement. Inlet flow rates and sulfur concentrations at the absorber inlet, in either case, are from 2005 data. These data are converted to inlet conditions as tons per day (tpd) of SO₂. Control efficiency, as obtained from vendors, is used to estimate emissions reductions as shown in the table. This description of the example table is generally applicable to all six tables in the confidential reports for Module 2.

SRU/TGTU

Several measures were examined for effectiveness across the refineries. To answer questions about how measures were selected for SRU/TGTU's, tables were constructed to show the measures identified as possible fits for each refinery and are shown in the Module 2 confidential appendices. Reductions in SO₂ and estimated cost effectiveness were inserted for each refinery, with the measure selected printed in bold type.

In three cases the recommended emission reduction measures have the combination of lowest cost and greatest quantity of SO₂ removed. In the remaining three cases the measures are chosen as the apparent best combination of high SO₂ removal and low cost.

G. RECAP OF DATA REQUESTS

Many technical data requests were issued to all of the refineries (and the AQMD) during the course of this study. The vast majority of them were made prior to the initial site visits by means of a comprehensive questionnaire. Each refinery responded to the questionnaire by furnishing tabulated data and reference drawings/documents. Likewise, they responded to the handful of post-visit requests with appropriate follow-ups. Specific details of the information requested and received can be found in the confidential appendices for each refinery.

APPENDIX A – DATA TABLES

TABLE A-1

Summary of Baseline Emissions, Emission Reductions, and Theoretical Remaining Emissions for Implementing Selected Measures in Module 2 and Module 3A

Part (a) – SO_x as of 2005 [tons per day (tpd)]

Refinery Number	1	2	3	4	5	6	Total
Process:							
FCCU	0.61	0.31	0.36	0.25	0.96	1.04	3.52
SRU & Tailgas	0.16	0.20	0.30	0.05	0.09	0.31	1.11
Others ¹ (by difference)	0.09	0.40	0.34	0.70	0.83	0.51	2.87
Total	0.86	0.91	0.99	1.00	1.88	1.86	7.50

Part (b) – Projected SO_x Reductions [tons per day (tpd)]

Refinery Number	1	2	3	4	5	6	Total
Process:							
FCCU	0.58	0.19	0.28	0.20	0.87	0.94	3.07
SRU & Tailgas	0.13	0.17	0.15	0.04	0.06	0.29	0.83
Others ²	0.06	0.07	0.04	0.35	0.33	0.04	0.89
Total	0.77	0.43	0.46	0.59	1.26	1.27	4.78

Part (c) – Theoretical³ Resulting SO_x [tons per day (tpd)]

Refinery Number	1	2	3	4	5	6	Total
Process:							
FCCU	0.03	0.12	0.08	0.04	0.09	0.10	0.45
SRU & Tailgas	0.03	0.03	0.15	0.01	0.04	0.02	0.28
Others ²	0.02	0.33	0.30	0.36	0.49	0.47	1.98
Total ⁴	0.09	0.48	0.53	0.41	0.62	0.59	2.72

Notes:

1. This includes boilers, heaters, furnaces, cogen plants, and other combustion units firing refinery fuel gas.
2. As in Note 1 above and enumerated in Matrix Table.
3. The measures in Modules 2 and 3A are not independent of one another, thus care was taken to arrive at the facility total.
4. Entries in the Part (c) table are the difference between Part (a) and Part (b) numbers.

TABLE A-2
Summary of Selected Measures, Emission Reductions and Average Cost Effectiveness

	REFINERY 1		REFINERY 2		REFINERY 3		REFINERY 4		REFINERY 5		REFINERY 6		TOTAL EMISSION REDUCTION	
	Reduction (TPY)	CE (\$/ton SOx)	Reduction (TPY)	CE (\$/ton SOx)	Reduction (TPY)	CE (\$/ton SOx)	Reduction (TPY)	CE (\$/ton SOx)	Reduction (TPY)	CE (\$/ton SOx)	Reduction (TPY)	CE (\$/ton SOx)	TPY	TPD
FCCU MEASURES													1,119.42	3.07
M1	211.82	\$14,437	69.76	\$76,211	103.56	\$36,636	74.54	\$42,103	317.60	\$11,600	342.14	\$12,849		
SRU/TGTU MEASURES													301.91	0.83
M13	46.78	\$22,410			53.00	\$12,881	13.69	\$54,686						
M16														
M17			61.38	\$39,000					20.75	\$123,186	106.31	\$36,359		
FUEL GAS SYSTEM MEASURES													323.39	0.89
M20							126.70	\$4,903			14.50	\$57,428		
M20B					12.84	\$46,905								
M20A									14.74	\$31,035				
M21B									106.20	\$19,688				
M21A			25.22	\$30,948										
M22	23.19	\$2,395												
HEATERS/BOILERS													N/A	N/A
None Selected														
TOTAL EMISSION REDUCTION (TPY)	281.79		156.36		169.40		214.93		459.29		462.95		1,744.72	
TOTAL EMISSION REDUCTION (TPD)	0.77		0.43		0.46		0.59		1.26		1.27		4.78	
COST EFFECTIVENESS ESTIMATION													Average CE for 6 Refineries	
Average Cost Effectiveness (\$/ton SOx Reduced)	\$14,770		\$54,303		\$29,982		\$20,975		\$36,025		\$19,644		\$25,533	

TABLE A-3**Measures for Controlling Refinery Fuel Gas - Example**

Measure	SO ₂ in, tpy	SO ₂ removed, tpy	Efficiency	PWV, millions of \$	Cost effectiveness, \$/ton removed	Recommended?	Notes
M20, Sulfinol on No. Q45 & Q64 H ₂ S absorbers	30.63	25.86	84.4	8.24	12,700	Yes – removes less SO ₂ than M21, but is nearly a quarter of the cost	Treats non-H ₂ S sulfur compounds, converts existing absorbers from amine, flow rate data given with 2005 concentrations of H ₂ S and non-H ₂ S compounds. Efficiency from vendor.
M21, Add Merox system to RFG line	40.7	37.0	91.0	43.0	46,500	No	Treats non-H ₂ S sulfur compounds with new absorber. Flow rate and Sulfur loadings available.